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COMBUSTION PRODUCT EVALUATION OF VARIOUS CHARGE SIZES AND PROPELLANT FORMULATIONS

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Task I Report:

SAMPLING AND ANALYTICAL PROCEDURES PROPOSED FOR USE IN GUN PROPELLANT COMBUSTION PRODUCT CHARACTERIZATION

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FOREWORD

In the program entitled "Combustion Product Evaluation of Various Charge Sizes and Propellant Formulation", the contract requires that a report be prepared as part of Task I, describing the proposed analytical and sampling procedures to be used on the program. This is that report. As a result of experience gained during the course of the program some of the sampling and analytical procedures may be modified. Comments and criticisms with respect to the proposed procedures will be welcomed.

Respectfully submitted,
IIT RESEARCH INSTITUTE

A. Snelson
Principal Investigator

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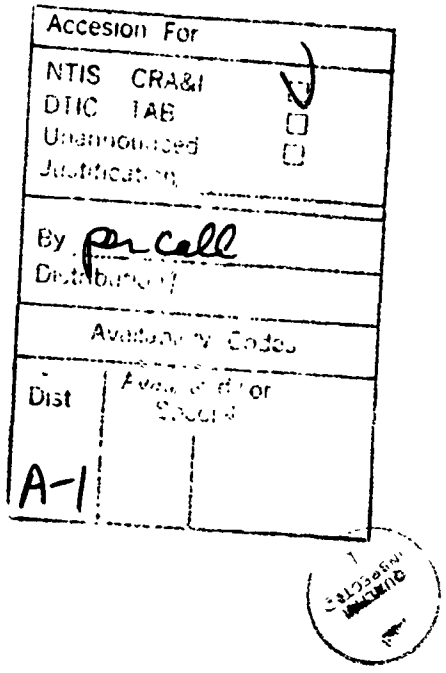

TABLE OF CONTENTS

1. INTRODUCTION

The sampling and analytical procedures described here are designed to satisfy the contractual requirements of the program entitled "Combustion Product Evaluation of Various Charge Sizes and Propellant Formulation" supported by the U.S. Army Medical Research and Development Command under contract number DAMD17-88-C-8006. The proposed sampling and analytical procedures are based on IITRI's prior experience in this technical area.[1,2] A primary object of the program is to relate the amount of combustion products formed to the unit mass of propellant burned. To do this, it will be necessary to relate the amount of material sampled and analyzed to the amount of CO, CO_2 and H_2 in that sample. The relative amounts of these three gases will be determined to establish the temperature at which equilibrium is frozen in the combustion products gases through thermodynamic equilibrium computer calculations on the combustion product composition for the specific propellant formulation used. An additional benefit of the proposed analytical scheme is that the amounts of all chemical species formed in the combustion products can be directly related to the amount of CO, CO_2 or H_2 present in the breech gas. Carbon monoxide concentrations are often monitored routinely when assessing health problems associated with weapon systems. Such data, when coupled with the chemical analyses derived in the program, will allow assessments to be made of likely operating personnel exposures to a large number of trace species.

Analyses will be made for the following chemical species that may be present in propellant combustion gases:

1) Gaseous aldehydes,
2) Polynuclear aromatic hydrocarbons,
   a) 4-6 ring PAHs
   b) methylated 3-4 ring PAHs
   c) nitro-PAHs.
3) Gas phase trace organics including mono and diaromatics.
4) Inorganic gases, including CO, CO_2, H_2, HNO_x + NO_x, HS_xO_y + SO_x, HCN, NH_3 and H_2S.
5) Metals (particulates).

Combustion gases will be sampled from the gun barrel, via the gun breech, and from spent casings. Since there are a number of difficulties associated with sampling from the spent casings in general, initial efforts will concentrate on the 105 mm shell casings for which the procedures are relatively straightforward. These results will then be used to direct future work in this area.

2. FIXTURES FOR COMBUSTION PRODUCT SAMPLING AND RELATED SAMPLING METHODOLOGY

In order to acquire combustion product samples from the gun barrel and spent shell casing, suitable adaptors will be fabricated for sampling purposes.

2.1 SAMPLING ADAPTORS TO EXTRACT RESIDUAL COMBUSTION PRODUCTS FROM THE GUN BARREL (Breech gas sampling)

From an initial visit to Aberdeen Proving Ground, the weapon systems shown in Table 1 were selected as potential candidates for combustion product sampling. These guns and typical rounds were visually inspected during this visit. From knowledge gained in this inspection, sampling adaptors to extract gun barrel combustion products were designed. These adaptors all utilize the shell casings or the cartridge used in the particular weapon system. They are shown in Figures 1-5. For sampling combustion products for inorganic gases, aldehydes and volatile trace organics, the sample will be extracted through a 1/8" OD Teflon tube (Figures 1, 2 and 5), the latter constructional material being used to minimize chemical reactivity of the sampling system with the combustion product gases. Although not shown in Figures 1, 2 and 5, a particle filter, Gelman glass fiber type A/E, 25 mm or 47 mm in diameter, will be attached to the Teflon sampling tube, exterior to the breech, to remove particulates from the gas stream prior to collection. It is anticipated that gas volumes in the range of ≃ 100 ml to 2000 ml will be extracted from the gun barrel, depending upon the specific analytical procedure requirements. Sampling times will be approximately 10 sec (inorganic gases and aldehydes) and from 0.5 - 8 mins (trace organics with Tenax collectors).

2.2 SAMPLING ADAPTORS TO EXTRACT RESIDUAL COMBUSTION PRODUCTS FROM THE GUN BARREL (Breech particulate and PAH sampling)

The adaptors to be used for particulates and PAH sampling are shown in Figures 3 and 4. The samples will be extracted through a 3/8" OD stainless steel tube directly into the collection system, (General Metal Works sampler for PAH and particulate collection). There will be no bends in the sampling

TABLE 1. BARREL VOLUME AVAILABLE FOR SAMPLING FOR VARIOUS GUN CALIBERS

Gun Typed (mm)	Breech Access	Barrel Length (cm)	Volume (liter)
25[1]	Poor [3]	218	1.07
105[2]	7 1/2" [4]	356	30.8
120	Good	533	60.3
155	Good	610	115.0
203 (8")	4"	803	260.0

[1]Program manager for this weapon indicated he would be willing to fire rounds specifically for our tests. Program managers for the remaining weapons indicated we would have to "piggy back" our experiments on their tests. It was subsequently found that this weapons is available with a manual loading breech to fine single rounds. In this guise it is known as the Mann barrel configuration. This would be the preferred configuration for breech gas sampling.

[2]This caliber gun is only available mounted in a tank. The remaining weapons are all available as field pieces (Howitzers) or mounted in test stands.

[3]The automatic round feeder makes access to the breech difficult. This weapon should probably be sampled from the muzzle.

[4]Length of restricted access area at breech end of gun.

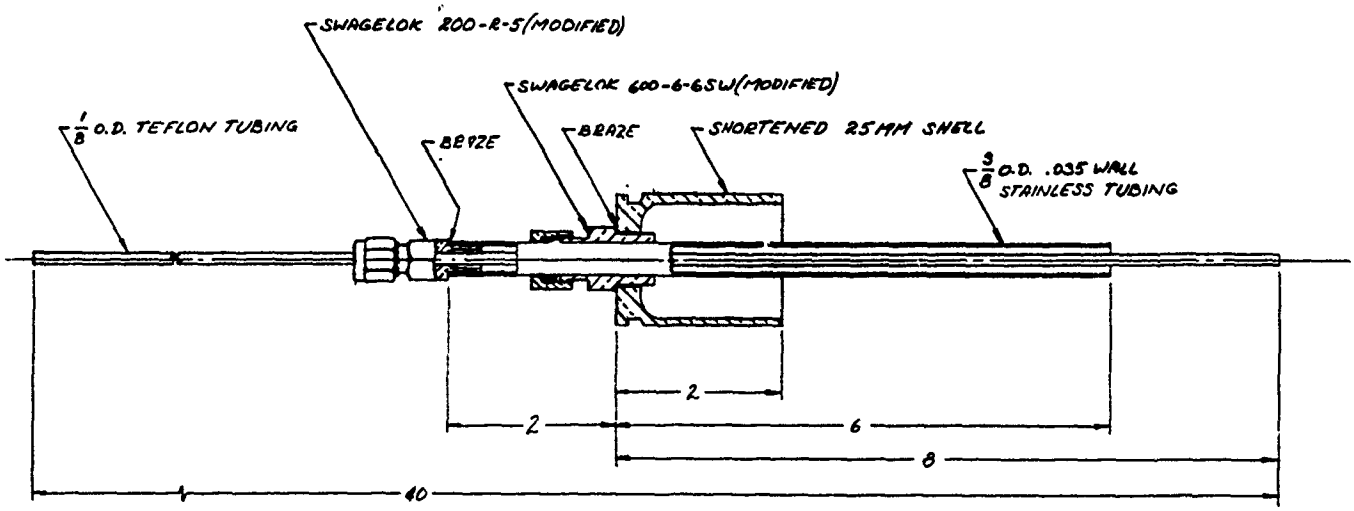

Figure 1. Engineering drawing of 25 mm caliber gun, breech sampling interface, for whole gas sampling (inorganic gases and aldehydes) and Tenax collectors (trace organic gases).

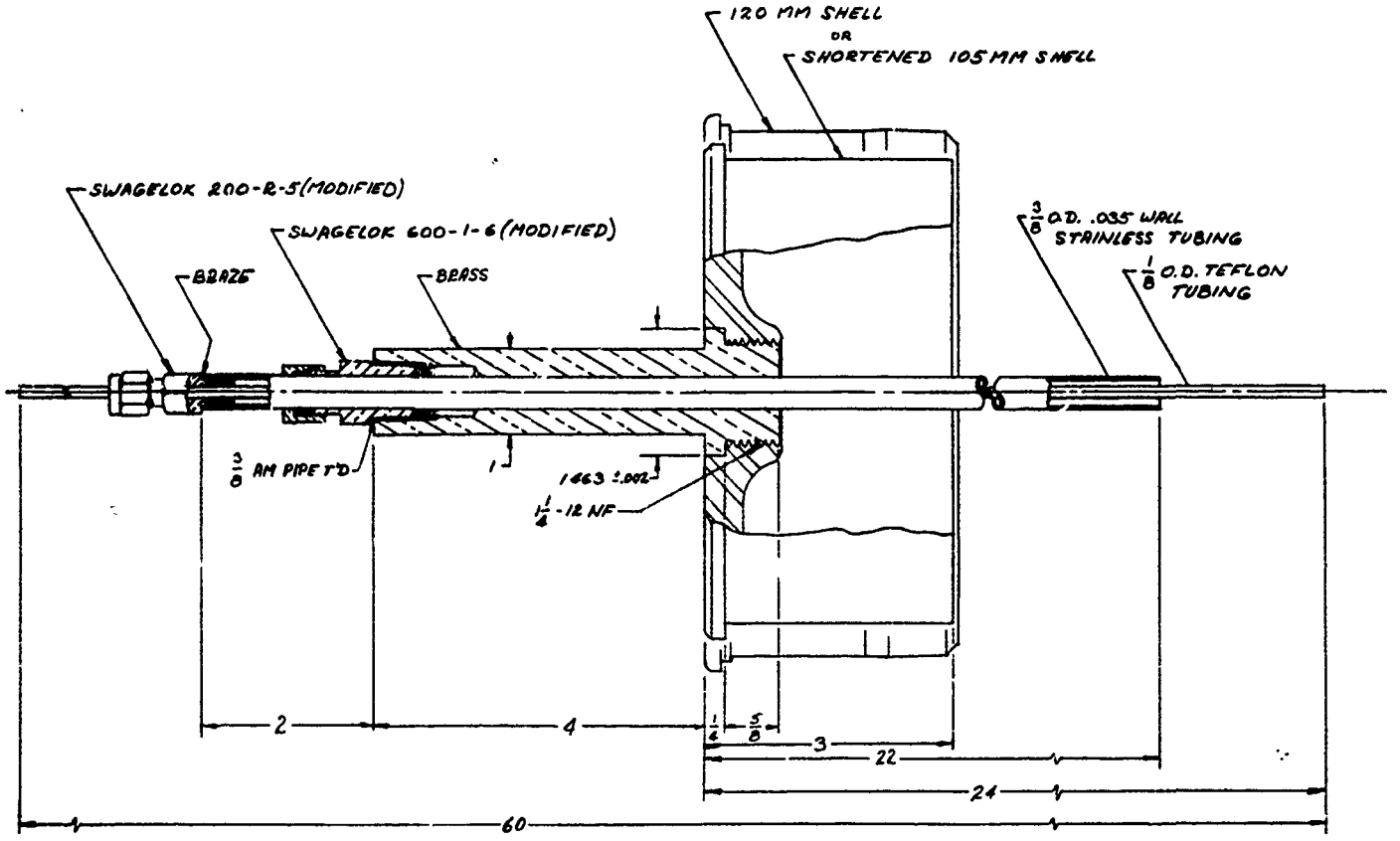

Figure 2. Engineering drawing of 105 and 120 mm caliber guns, breech sampling interface, for whole gas sampling (inorganic gases and aldehydes) and Tenax collectors (trace organic gases).

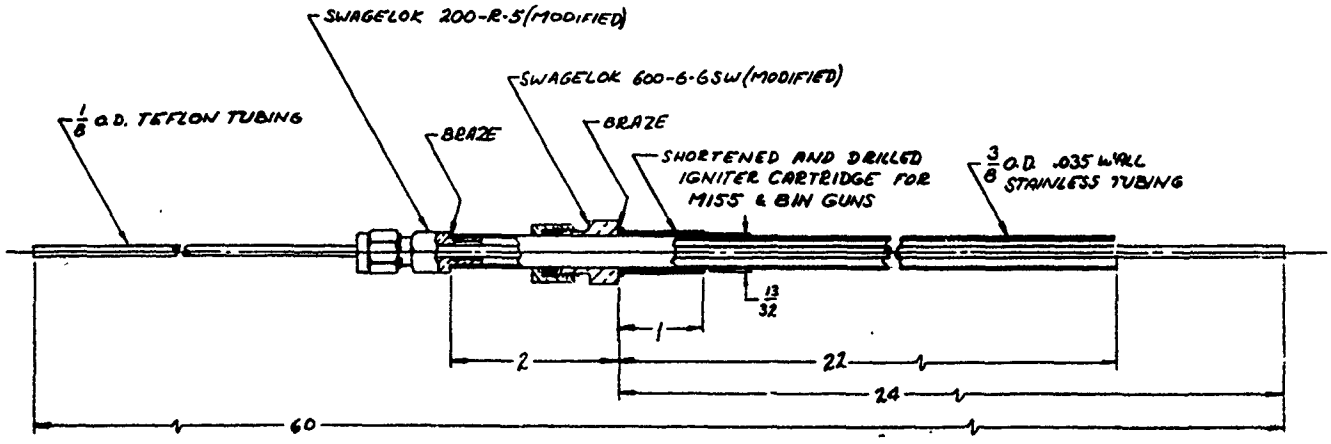

Figure 3. Engineering drawing of 155 mm and 8 in. caliber guns, breech sampling interface, for whole gas sampling (inorganic gases and aldehydes) and Tenax collectors (trace organic gases).

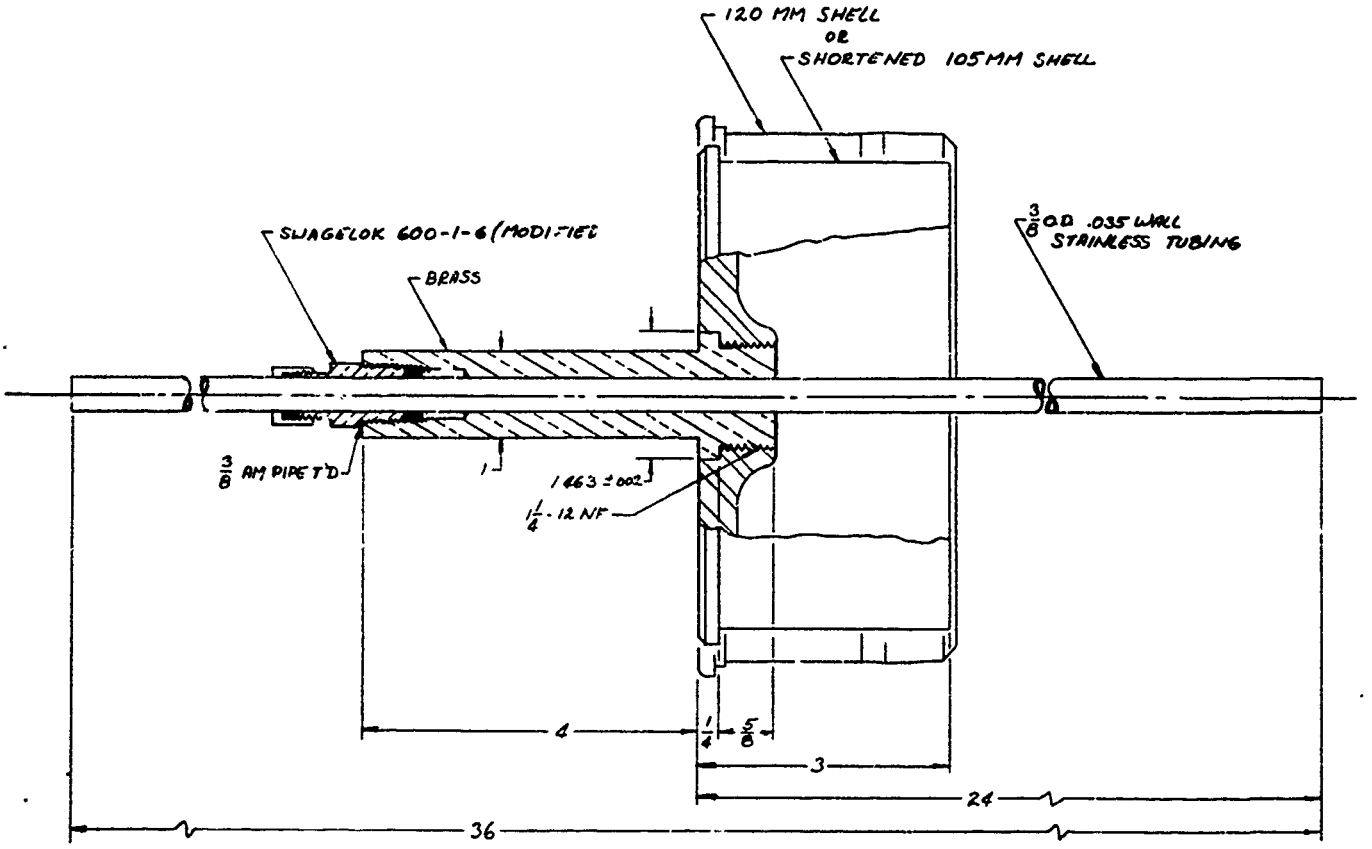

Figure 4. Engineering drawing of 105 and 120 mm caliber guns, breech sampling interface, for PAH and particulate collection.

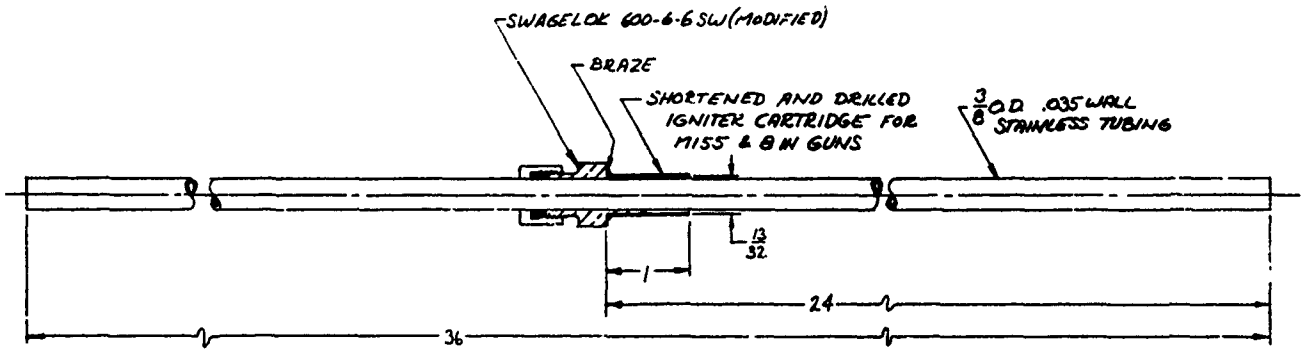

Figure 5. Engineering drawing of 155 mm and 8 in. caliber guns, breech sampling interface, for PAH and particulate analyses.

line to minimize loss of aerosols by impaction on surfaces. A minimum of 30 liters (PAHs) and 10 liters (Metals) of combustion gases will be extracted at 10 liters/min. Based on initial experimental results, these sample sizes may be decreased or increased appropriately.

2.3 SAMPLING ADAPTORS TO EXTRACT RESIDUAL COMBUSTION PRODUCTS FROM 105 mm SPENT SHELL CASINGS

This adaptor is shown in Figure 6 and is designed to be a snug fit on the end of the 105 mm spent shell casing. Due to the limited volume of combustion product gases contained in the casing ($\simeq$ 18 liters), samplings will only be made for the purpose of making inorganic gases, aldehydes and trace organics analyses.

2.4 GENERAL PROCEDURES FOR USING THE SAMPLING ADAPTORS

The breech adaptors will be housed in suitable containers at the gun site to maintain cleanliness. As soon as possible after firing the weapon, a polyethylene bag will be placed over the muzzle of the weapon and lightly secured to prevent undue egress of hot combustion products from the gun barrel. The spent shell casing will be slowly removed from the barrel and sealed with heavy aluminum foil sheets to prevent loss of combustion products. Immediately, on complete removal of the spent shell casing, the breech adaptor will be inserted into the barrel in readiness for sampling.

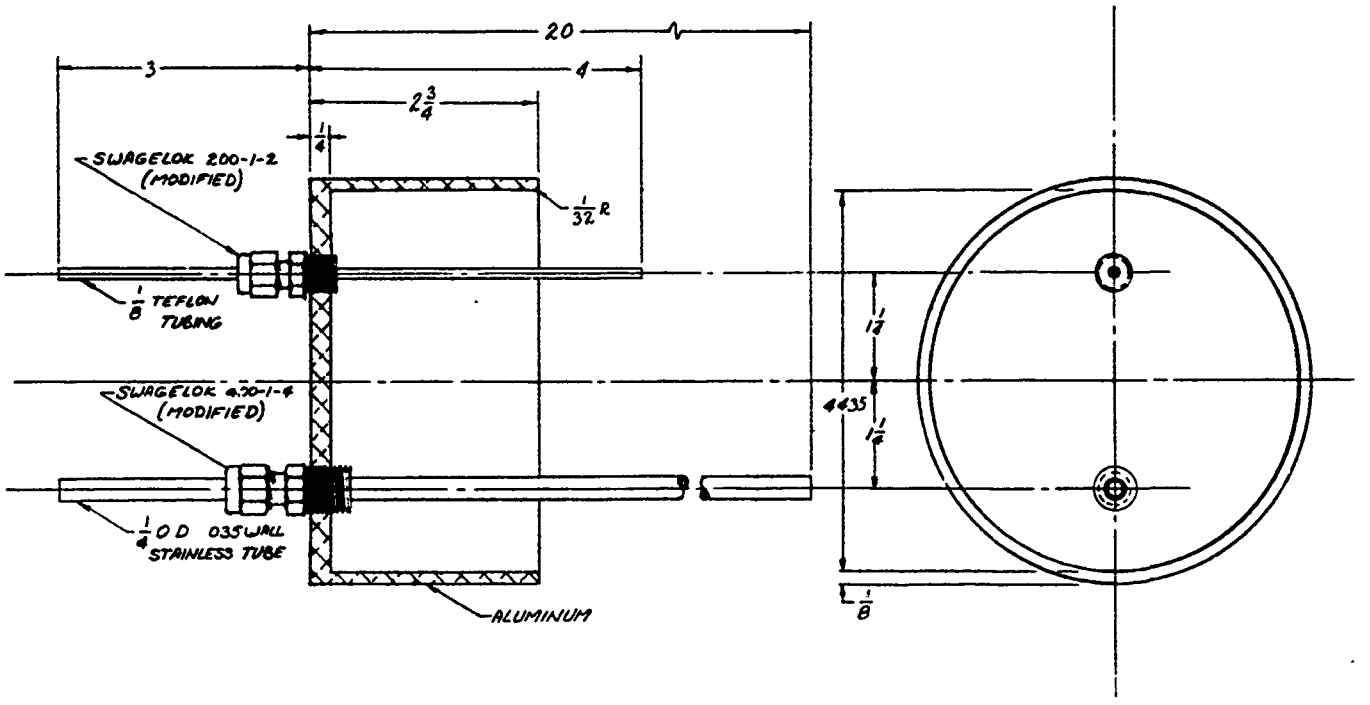

Figure 6. Engineering drawing of spent casing sampling interface, for a 105 mm round. This will be used for sampling inorganic gases, aldehydes and trace organic species from the casing.

3. SAMPLING AND ANALYTICAL PROCEDURES

An abbreviated overview of the proposed sampling an analytical procedures is presented in Table 2. Specifics of the procedures follow.

3.1 INORGANIC GASES. CO, CO_2, H_2, NO_X, SO_X, NH_3 HCN AND H_2S AND GASEOUS ALDEHYDES

3.1.1 Sampling for Inorganic Gases

All these gases will be sampled using an all glass/Teflon system to minimize possible sample loss. Prior experience indicates that a 1 liter sample of combustion gas, in conjunction with the analytical procedures to be used, will allow detection of all gases except CO, CO_2 and H_2 at the $\leq$ 0.1 ppm level in the concentrated combustion gases in the barrel. The detection limit for CO, CO_2 and H_2 is $\simeq$ 250 ppm. However, these gases are present in the sample at the 10^5 ppm level.

The combustion gases will be sampled into evacuated 1 liter glass flasks and then stored for transportation to IITRI. Each flask is fitted with a silicone rubber/Teflon septum and a Teflon-viton O-ring, high vacuum stockcock. Prior to sampling the combustion gases, the flasks will be evacuated at the gun site with a mechanical oil vacuum pump, fitted with an oil vapor/particle filter. The pressure in the system will be monitored with a 0-5000 µm Hg thermocouple gauge during the evacuation procedure. All flasks will be evacuated to $\leq$ 500 µm Hg prior to use. Each flask in turn will be attached to an all Teflon filter holder, containing a glass fiber filter, which in turn will be connected to the breech sampling line. Combustion gas samples will be obtained for HCN, NH_3, NO_x, SO_x, H_2S, and aldehyde analyses, where possible from the same gun firing. Immediately after sampling, suitable reagents will be added to each flask via syringe injection through the septum. These reagents and their amount are listed in Table 3. A total of five samples and one blank will be obtained for each analyte. The flasks used for the H_2S and aldehyde analyses will be kept in the dark as much as possible prior to their chemical analyses in Chicago. The flasks will be shipped by commercial truck to Chicago in wooden crates.

TABLE 2. ESTIMATED SAMPLING VOLUME REQUIREMENTS AND ANALYTICAL PROCEDURES FOR GUN SMOKE EVALUATION

BREECH SAMPLES							SPENT CASINGS	
Inorganic Gases			Volatile Organics	Aldehydes	PAH + Nitro PAH	Particulates	Inorganic Gases + Aldehydes	Tenax/GC
Species	Sample Size (liters)	Analytical Method						
CO	1	GC Thermal	Tenax Collector 1.5 g absorbent	1 liter of gas collected in evacuated glass flasks (same as inorganic gases) 2:4 DNPH + HPLC analysis	Combined filter + adsorbent Sample size >50 liters collected at ≈10 liters/min	Filters Sample size 10 liters	Sample sizes same as for breech analyses	
CO_2	1	Conductivity						
H_2	1	Detector						
NOx	1	NaOH + H_2O_2 Oxidation	Two nominal sample sizes ~100 ml and ~1,000 ml		Volume sampled controlled by critical orifice and measured by dry test meter	Volume sampled controlled by critical orifice and measured by dry test meter		
SOx		Ion Chromatograph						
NH_3	1	H_2SO_4 Nesslers Reagent Spectrophotometric	Sampling rate 200 ml/min controlled by rotameter flowmeter. Gas volume sampled, define by evacuated flasks.		Filter particulate analyzed for non-volatile PAHs and Nitro PAHs using HPLC	3 metals analyzed by AA		
HCN	1	NaOH Ion Specific Electrode						
H_2S	1	$Cd(OH)_2$ STRectan 10 Spectrophotometric			Adsorbent analyzed for volatile PAH by GC/MS			
All above samples collected in 1 liter evacuated glass flasks, Each flask contains 1 high vacuum stopcock and rubber septum			GC/MS Analysis					

TABLE 3. REAGENTS TO BE ADDED TO COMBUSTION PRODUCTS SAMPLED INTO 1 LITER GLASS FLASK

Analyte	Reagent
HCN	10 ml, 0.01N, NaOH
NH_3	10 ml, 0.01N, H_2SO_4
NO_x + SO_x	10 ml, 0.01N, NaOH + 1 ml 30% H_2O_2
H_2S	10 ml. 0.01M $CdSO_4$ + STRactan 10 in H_2
Aldehydes	10 ml of 3.1 µM/ml 2.4-dinitrophenylhydrazine (DNPH) soln. in acetonitrile + 5 drops 1N, $HClO_4$

3.1.2 Analytical Procedures for Inorganic Gases and Aldehydes

3.1.2.1 CO, CO_2 and H_2

A 1 ml gas sample will be removed from each flask and analyzed on a Carle Model 111-H 196A gas chromatograph, fitted with thermal conductivity detectors. Two samples will be extracted from each flask and analyzed for the three gases. The GC will be calibrated against a Matheson Certified Gas Standard; CO_2, 8%; H_2, 12%; CO, 15%; balance, N_2. The instrument calibration will be verified each day.

3.1.2.2 HCN

The alkaline aqueous solution of cyanide will be washed out of the flask with three 15 ml aliquots of distilled water into glass-Teflon sealed bottles. These samples will be analyzed for cyanide [3] ion at TEI Analytical of Niles, Illinois using an EPA approved method. The method is presented in detail in Appendix I.

3.1.2.3 NH_3

These samples will be removed from the flasks as in (2) above and sent to TEI Analytical for analyses by an EPA approved procedure [4]. This is presented in detail in Appendix I.

3.1.2.4 $NO_x + SO_x$

This analytical procedure is based on the alkaline hydrogen peroxide oxidation of NO_x and SO_x to nitrate and sulfate ions.[5,6]. The aqueous solutions will be washed from the flasks as described above into 250 ml beakers. Excess H_2O_2 will be removed by adding ≈ 0.0 1g of MnO_2 to the solution and boiling for 15 minutes. On cooling, the solutions will be filtered, made up to 100 ml and analyzed with appropriate dilution on a Dionex System 14 ion Chromatograph.

3.1.2.5 H_2S

These samples will be removed from the flasks as indicated above. The collected CdS will be determined spectrophotometrically by measurement of the methylene blue produced by the reaction of N,N-dimethyl-p-phenylenediamine and ferric chloride as described in the NIOSH Manual of Analytical Methods (presented in Appendix 1).

3.1.2.6 Aldehydes

After sampling, the 1ℓ flasks will be injected with 10 mℓ of a 3.1 μM/mℓ 2,4-dinitrophenylhydrazine (DNPH) solution in acetonitrile containing five drops of IN $HClO_4$ catalyst added just prior to injection. The flasks will be stored in the dark until analysis. Upon return, samples will be analyzed as soon as possible. The liquid will be drawn off and the flask washed three times with 10 mℓ of acetonitrile each. The combined acetonitrile DNPH solution will be filtered over 20 grams of anhydrous sodium sulfate, concentrated to dryness at 40°C under argon, and the residue redissolved in 1.0 mℓ of acetonitrile for analysis.

The samples will be analyzed using a reverse phase HPLC system as described for the PAH analysis. The samples will be eluted on a 4.6 mm x 25.0 cm Zorbax ODS column and the components monitored with a Kratos Model 783 spectroflow programmable absorbance detector at 365 nm. The sample will be eluted using the following solvent conditions. Acetonitrile/water 50%/50% for 10 min followed by a gradient to 100% acetonitrile in 25 min. The samples will be quantitated by the external standard method using aldehyde hydrazones available at IITRI. Formaldehyde, acetylaldehyde, acrolein, propionaldehyde, crotonaldehyde, isobutylaldehyde, benzaldehyde, and hexylaldehyde will be determined. The limit of detection for these compounds is approximately 200 ng per sample.

3.2 GAS PHASE ORGANICS, POLAR CONSTITUENTS, MONO AND DIAROMATICS BY GC/MS

3.2.1 GC/MS Sampling for Trace Organic Species

With the exception of the diaromatics, these species will be sampled using Tenax collectors. A schematic diagram of the sampling arrangement is shown in Figure 7. The volume of gas sampled will be controlled by fully or partially evacuating one of the metal flasks shown in Figure 7. The evacuated flask will be opened to the sampling line and the gas flow through the Tenax collector limited to <200 ml/min by a needle valve mounted on the rotameter flow meter. With this system, the volume of gas sampled may be varied between 0-275 ml or 0-2200 ml. Previous experience indicates that gas volumes of ≈100-200 ml and 1000-2000 ml should be sampled and collected separately for GC/MS analyses to ensure suitably sized samples for good analyses of the more

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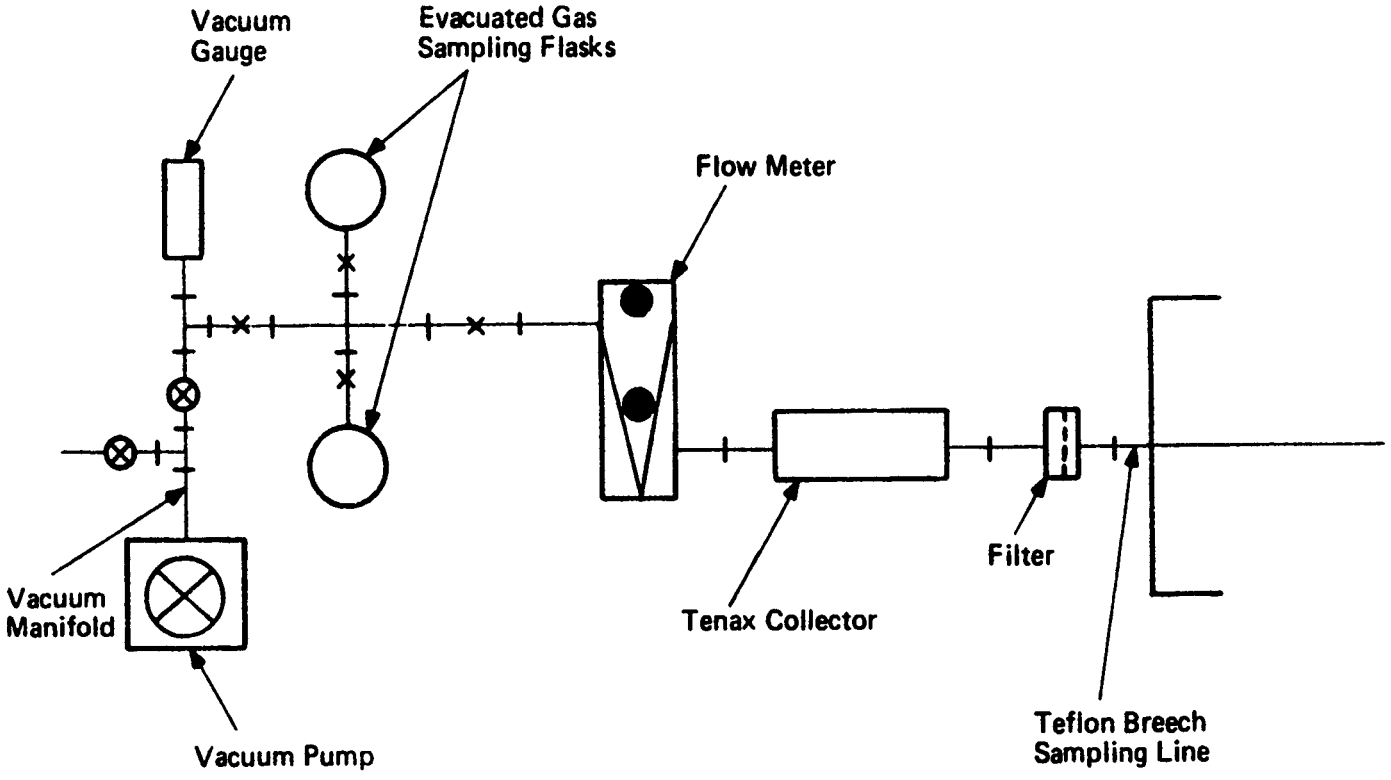


Figure 7. Schematic diagram of the combustion gas sampling line when using Tenax collectors for trace organic species.

and less abundant species without saturating the MS detection system. In each series of experiments (gun systems sampled), two Tenax samplers in series will be used when collecting the first small and large gas samples, to test for collector overloading and breakthrough.

Five each of the smaller and larger samples will be collected together with one blank for each. The metal flasks containing the nonadsorbed combustion gases will be returned to IITRI for CO, CO_2, and H_2 analyses.

The diaromatics will be collected using the General Metal Works sampler for PAH sample acquisition. This system is described in the next section and will not be discussed further here.

3.2.2 Preparation of Tenax Collectors

Tenax cartridges will be prepared by a method based on that described by Bumgarner [7]. The Tenax will be cleaned by successive Soxhlet extractions in methanol and in pentane, for 24 hours each, to remove soluble contaminants. After extraction, the Tenax will be removed from the Soxhlet thimble, placed in an open Pyrex dish, and dried under an infrared lamp. After 2 hours, the Tenax will be moved to a vacuum oven (100°C, 2 hours, 2-3 ml helium flow). Upon removal from the oven, the Tenax is sieved (40/60 mesh) into a clean beaker.

Glass cartridges, as well as the culture tubes and their Teflon-lined caps which will be used to store the cartridges, will be washed with detergent and water in an ultrasonic bath for 30 minutes. After rinsing and drying, clean Tenax (≈1.5 g) will be packed in the cartridges and held in place with glass wool plugs. The cartridges will be placed in individual culture tubes and stored under refrigeration until used for sample collection and analysis. Prior to use, the cartridges will be placed in a bakeout chamber and purged with clean helium at a flow rate of 100 ml/min for 2 hours at 250°C. The samplers will be cooled in the precleaned culture tubes, which will be sealed to prevent contamination during storage and transportation to/from the sampling site. Normally, one or two cartridges in each batch are designated as blanks in order to assess the occurrence and degree of any contamination.

3.2.3 Sample Transfer and GC/MS Analysis

The air samples will be stripped from the cartridges by thermal desorption and purged with helium into liquid-nitrogen cooled cyrotrap (Tekmar 5010 thermal desorption unit). The trap will be rapidly heated and the compounds flushed onto a high resolution GC column, to separate the components. Identification and quantification is achieved by mass spectrometric measurement of the total ion current signal followed by computer enhancement of the raw GC/MS data. (Quantitative data may be obtained as long as the breakthrough volume of the component is not exceeded during sampling.)

Certain organic species, detected in the combustion products from all five weapons systems tested, will be targeted for quantification. Since this selection cannot be made until all weapon systems have been sampled and qualitatively analyzed, each Tenax collector, prior to analyses, will be spiked with two internal standards (octafluorotoluene and pentafluorobromobenzene) to enable subsequent quantitative analyses to be made on the targeted compounds.

Samples will be analyzed on a 25m CPWax 52CB chemically-bonded fused-silica thick-phase capillary column, with a carrier gas flow rate of about 1 ml/min. The column will be initially held at a temperature of 25°C for 5 minutes, then heated at 4°C/min t 210°C. The column is coupled directly to the ion source of the mass spectrometer. The mass spectrometer, a Finnigan MAT 311A, will be scanned from m/e 20 to m/e 250 every 2.2 sec during the run, and the data acquired in this way will be stored by computer on a disk using a SpectroSystem MAT SS-200 data system.

Characterization of the components in the sample will be greatly improved by subjecting the raw acquired data to a computer-based enhancement algorithm. This CLEANUP program automatically locates components in successive time windows and products a set of "clean" spectra freed of background contributions and peaks from unresolved components. The "clean" spectra are then used for qualitative and quantitative characterization. Identification is established either by means of computer-based library search routines or manually from tabular data.

Ideally, quantification should be carried out by first preparing calibration curves for each compound of interest. For reasons noted above, this will not be the procedure used here. Instead, a method will be used based on the "clean" peak area data generated by the CLEANUP program, and response factors which obviate the need for complete calibration curves for each compound. Relative concentrations and relative retention data will be generated with respect to the internal standards already noted. The response factors will be used to establish the relationship between relative concentration and the actual amount of material present in the sample. The factors will be obtained in separate experiments using known amounts of targeted components and standards in synthetic mixtures and running them under the same conditions used for the samples.

The compounds of interest in the sample will be sought finally and quantified using an automated matching program. Each spectrum in the sample file will be matched against a library of targeted compounds, in preset elution time windows. Scoring will be based on the similarity of spectral data within each window. Once a peak of interest has been "flagged" in the sample file, the program uses the information on the substance (response factor, molecular weight, etc.) stored in the computer to calculate the amount present.

Samples containing diaromatic compounds collected in the PAH sampler will be analyzed using essentially the same GC/MS techniques described above.

3.3 POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) AND NITRO-PAHs

3.3.1 Sampling for PAHs and Nitro-PAHs

A schematic diagram of the sampling system for PAHs collection is shown in Figure 8. Details of the General Metal Works (GMW) PAH collector are presented below. In initial experiments, a minimum of 30 ℓ of combustion gas will be sampled through the GMW collector at a flow rate of ≈10 ℓ/min. The sampled gas volume will be measured with a dry test meter. The total volume of gas sampled will be collected in a Tedlar bag. After collecting the gas sample, the Tedlar bag will be agitated to mix the contents, a representative sample of gas withdrawn into an evacuated metal flask ≈275 ml, and the latter returned to IITRI for CO, CO_2, and H_2 analyses. The polyurethane foam and

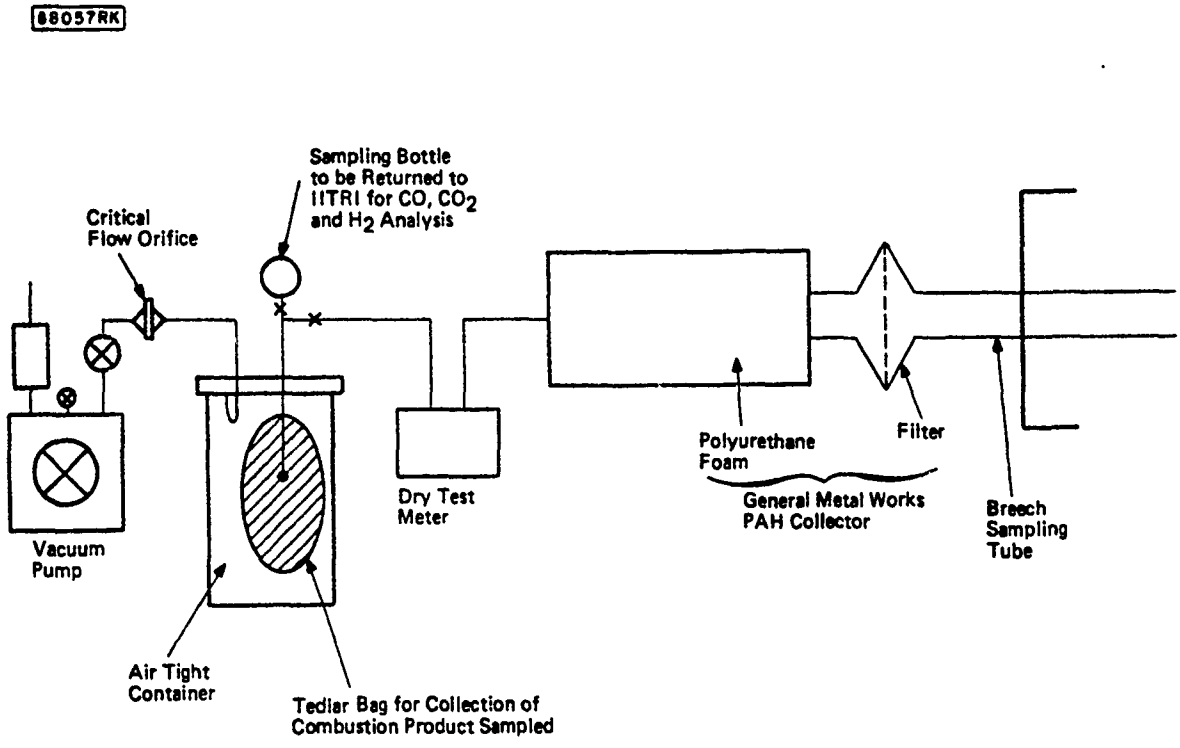


Figure 8. Schematic diagram of the combustion gas sampling line when using the General Metal Works sampler for PAH collection.

filter will be removed from the GMW collector and returned to IITRI for analyses. In one experiment, two GMW collectors will be used in series to test for sample breakthrough. For each gun system, five samples will be collected for analyses together with one ambient air blank.

3.3.2 GMW PAH Collector and Collector Preparation

PAH samples will be collected using a General Metal Works (GMW) PS-1-1 Sampler, which consists of an upper compartment containing a 102 mm Pallflex© TX40H120WW Teflon coated glass fiber filter to collect the particulate material (Figure 8). The vapor phase PAH are collected in the lower compartment which holds a glass cartridge containing a 78 mm x 63 mm polyurethane foam (PUF) plug. Prior to sampling, the PUF plug is placed in the glass cartridge and pretreated by extracting for 24 hours in methylene chloride. The assembly is dried in a vacuum drying oven overnight, wrapped in aluminum foil, and placed in a glass jar under argon. The plug assembly will be inserted into the PS-1-1 sampler immediately prior to obtaining a sample. After sampling, the filter will be removed, covered with a second filter, and placed in a labeled glass petri dish. The PUF plug assembly will be replaced in the same glass jar purged with nitrogen.

3.3.3 PAH Analysis by HPLC

The polycyclic aromatic hydrocarbons (PAH) that will be measured in this study are phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pryene, benzo[e]pyrene, and benzo[g,h,i]perylene. These materials were selected based on their known presence in Diesel exhausts and their availability as "standard material" from NBS.

The filter and PUF plug assemblies from the GMW sampler will be extracted separately for eight hours in methylene chloride and the extracts combined. The combined extract will be concentrated under a gentle stream of argon at 30°C to 1 mℓ. The sample will be solvent exchanged to hexane by combining the methylene chloride extract with 4 mℓ of hexane in a Kuderna-Danish concentrator tube with a Micro Snyder column. The sample will be heated to 66°C in a water bath for 20 minutes or until the volume has been reduced to under 4 mℓ. The hexane extract will be concentrated to ~400 µℓ under argon and the volume brought to exactly 1,000 µℓ with hexane. Half of this latter extract will be analyzed by GC/MS for one and two ring PAH's.

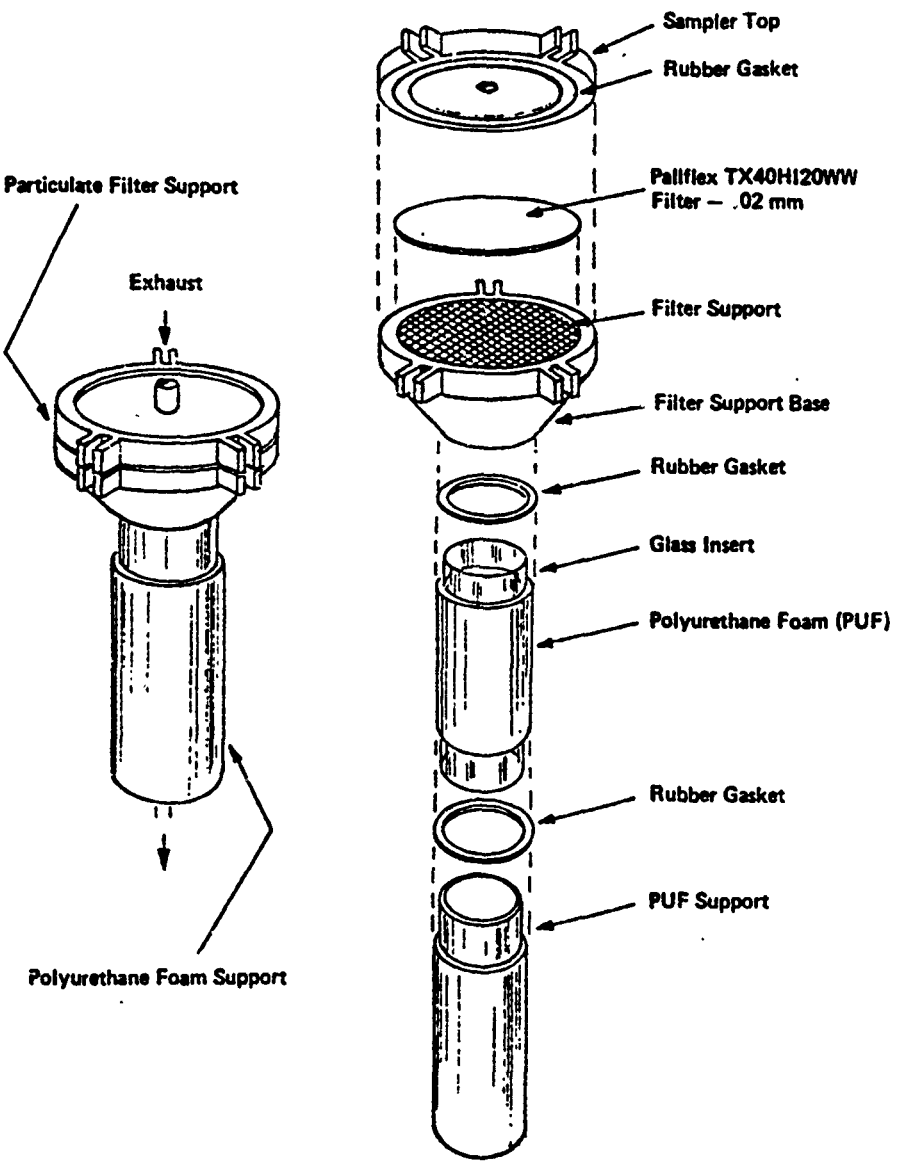


Figure 9. General Metal Works sampler for PAH collection.

The extract (100 µℓ) will be fractionated on a Water's bondapac NH_2 semipreparative HPLC column 7.8 mm x 30 cm using a solvent composition of 96% hexane, 4% methylene chloride, at a flow rate of 3 mℓ/min. The elution will be monitored with a UV-detector at 254 nm. Three fractions will be obtained. The first fraction will contain PAH's of three rings or less, the second PAH's of four rings, and the final fraction will contain five or more ring PAH's (Table 4). A standard containing pyrene and chrysene, the first and last eluting PAH of the second fraction, respectively, will be run prior to each sample to determine the exact fraction cut times. Each fraction will be concentrated under argon at 30°C to 1 mℓ and solvent exchanged to acetonitrile at 85°C. The samples in acetonitrile will be concentrated to a final volume (100 µℓ to 1.0 mℓ) depending on the level of PAH present.

All PAH sample analyses will be performed on a Water's HPLC system consisting of two Model 6000A pumps, a Model 712 wisp auto injector, and a Model 730 system controller coupled to a Model 720 data module. The samples will be eluted on a 4.6 mm x 25 cm Vydac 201 TP 5 micron reverse phase HPLC column with an acetonitrile/water gradient. Detection will be accomplished using a Kratos Model 980 programmable fluorescence detector. Tables 5 through 7 detail the information concerning the analyses of PAH fractions 1 through 3, respectively. All samples will be quantitated by external standard method using the National Bureau of Standards' PAH Standard, SRM 1647. Since the standard does not contain benz[e]pyrene, this material will be prepared separately in acetonitrile and the SRM 1647 will be diluted into this solution. Peak identification will be made using retention times.

3.3.4 Nitro PAH Analyses by HPLC

Samples obtained for PAH analyses will also be analyzed for nitro-PAH. The following compounds will be determined; 9-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, 7-nitro benz[a]anthracene, 6-nitrochrysene, and 6-nitrobenz[a]pyrene. Samples may also be analyzed for the highly mutagenic dinitropyrenes 1,3-dinitropyrene, 1,6-dinitropyrene, and 1,8-dinitropyrene should significant levels of 1-nitropyrene be found. Due to the extensive sample preparation involved, dinitropyrenes will be excluded from analysis initially. Sufficient sample will be retained to ensure these analyses can be performed if required.

TABLE 4. ELUTION OF POLYCYCLIC AROMATIC HYDROCARBONS ON A BONDAPAK NH_2 COLUMN[a]

PAH	Relative Elution Time	Fraction[b]
Anthracene	0.76	Fraction 1
Phenonthracene	0.80	
Pyrene	1.00	Fraction 2
Fluoranthene	1.02	
Benz[a]anthracene	1.44	
Chrysene	1.46	
Benzo[k]fluoranthene	1.73	Fraction 3
Benzo[b]fluoranthene	1.89	
Benzo[a]pyrene	1.84	
Benzo[e]pyrene	2.26	
Benzo[ghi]perylene	2.56	

[a] HPLC conditions: N Bondapak NH_2 column 7.8 mm x 30 cm; hexane: methylene chloride 96:4 at 3.0 mℓ/min, run time 60 min. The column is back-flushed at this time by reversing the solvent flow using a Model 721 Rheodyne valve and running a linear gradient to 100% methylene chloride at 10% per minute. The methylene chloride flow is continued for 10 min and then an identical reverse gradient to 100% hexane is run. At 100% hexane, the system is allowed to equilibrate for 15 min. The frequency of using the back-flush depends on the nature of the sample.

[b] The fraction cut times may vary depending on various factors, e.g., the volume, its conditioning, etc., so it is important to run the PAH column standard before each fractionation.

TABLE 5. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS: ELUTION SCHEME 1[a]

PAH	Retention Time, min	Fluorescence Wavelength, nm		Detection Limit,[c] ng
		Excitation	Emission[b]	
Phenanthrene	19.56	260	370	0.296
Anthracene	21.00	260	370	0.153

[a] HPLC elution conditions: 4.6 mm x 25.0 cm Vydac 5 micron reverse-phase column; linear gradient, acetonitrile/water (50/50, V/V) to acetonitrile/water (70/30, V/V) in 30 min then to 100% acetonitrile in 10 min followed by 10 min at 100% acetonitrile. The system was returned to initial conditions using a reverse gradient of 5%/min of 10 min and equilibrated at initial conditions for 15 min; flow: 1.0 mℓ/min, injection volume: 30 µℓ.

[b] A detector with a 370 nm emission cutoff filter was used.

[c] The detection limit was defined as the on-column amount of compound that would give a peak that was five times the baseline noise under these instrumental conditions.

TABLE 6. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS: ELUTION SCHEME 2[a]

PAH	Retention Time, min	Fluorescence Wavelength, nm		Detection Limit,[c] ng	Elution Scheme
		Excitation	Emission[b]		
Fluoranthene	10.88	260	370	0.129	2a
Pyrene	12.24	260	370	0.187	2a
Benz[a]anthracene	18.26	260	389	0.0368	2b
Chrysene	20.10	260	370	0.0519	2a

[a] HPLC elution conditions: 4.6 mm x 25.0 cm Vydac 5 micron reverse-phase column; isocratic elution, acetonitrile/water (70/30, V/V) for 15 min then a linear gradient to 100% acetonitrile in 15 min followed by 15 min at 100% acetonitrile. The system was returned to initial conditions using a reverse gradient of 5%/min of 10 min and equilibrated at initial conditions for 15 min; flow: 1.0 mℓ/min, injection volume: 30 µℓ.

[b] A detector with a 370 and 389 nm cutoff filter was used in these analyses.

[c] The detection limit was defined as the on-column amount of compound that would give a peak five times the baseline noise under these instrumental conditions.

TABLE 7. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS: ELUTION SCHEME 3[a]

PAH	Retention Time, min	Fluorescence Wavelength, nm		Detection Limit,[c] ng
		Excitation	Emission[b]	
Benz[e]pyrene	32.28	280	389	0.142
Benzo[b]fluoranthene	33.16	280	389	0.0278
Benzo[k]fluoranthene	35.24	280	389	0.0124
Benz[a]pyrene	36.82	280	389	0.0184
Benzo[ghi]perylene	42.01	280	389	0.109

[a] HPLC elution conditions: 4.6 mm x 25 cm Vydac 5 micron reverse-phase column; linear gradient, acetonitrile/water (50/50, V/V) to acetonitrile in 40 min followed by 20 min at 100% acetonitrile. The system was returned to initial conditions using a reverse gradient of 5%/min of 10 min and equilibrated at initial conditions for 15 min; flow: 1.0 mℓ/min, injection volume: 30 μℓ.

[b] A detector with a 389 nm cutoff filter was used.

[c] The detection limit was defined as the on-column amount of compound that would give a peak five times the baseline noise under these instrumental conditions.

A 200 µℓ portion of the hexane extract from the PAH analysis will be fractionated on a 7.8 mm x 30 cm bondapak NH_2 column. An isocratic elution of 90% hexane/10% methylene chloride at 1.5 mℓ/min will be used to elute the extract. The nitro-PAH fraction elutes in the area of 12-20 min and will be monitored by a UV absorbance detector at 254 nm. A standard of the nitro-PAH material will be run prior to each field sample to determine the exact fraction collection time. The nitro-PAH fraction will be concentrated under argon at 30°C in the dark and solvent exchanged to acetonitrile at 85°C. The acetonitrile will be concentrated to a final volume of 200 µℓ for analysis.

The nitro-PAH samples will be analyzed by reverse phase HPLC employing on column reduction of the nitro group to the highly fluorescent amino derivative. A Water's HPLC system, as described previously, will be used. The column arrangement consists of a particulate filter, a 4.6 mm x 15 cm Zorbax ODS column, a catalytic column containing a three-way catalyst (typical of automobile catalytic converters), and a second 4.6 mm x 15 cm Zorbax ODS column. The catalytic column is heated to 70°C. The samples are eluted using a gradient of methanol/water adjusted to Ph=8.0 with sodium hydroxide, at a flow rate of 1.0 mℓ/min. Detection of the resultant amino-PAH is accomplished using a Krotos spectroflow 980 programmable fluorescence spectrophotometer.

3.4 PARTICULATE METALS--THREE TO BE SELECTED

3.4.1 Sampling Procedure for Metals

Essentially the same system as described for collection of PAH samples will be used for collecting samples for metal particulate analyses. The only major exceptions will involve removal of the polyurethane form from the GMW collector and use of an S and H acid washed high strength glass fiber filter, type 1HV, in place of the Pallflex filter used in the PAH analyses. Again, 30 ℓ of combustion gases will be sampled at ≈10 ℓ/min. Five samples and one blank (particulates and gas samples) will be returned to Chicago, the particulates for analyses at TEI Analytical and the gas samples for analysis at IITRI.

3.4.2 Analytical Procedure for Metal Particulates

Analyses for the three selected metals will be made by TEI Analytical of Niles, Illinois, using inductively coupled plasma-atomic emission spectroscopy. Details of the filter extraction and analytical procedures are presented in Appendix 1.

REFERENCES

1. Characterization of Combustion Products of Military Propellants, Volumes 1 and 2. Final Report on Contract Number DAMD17-80-C-0019, prepared for U.S. Army Medical Research and Development Command, Fort Detrick, MD 21701-5012, March 1983. Prepared by A. Snelson, P. Ase, W. Bock, and R. Butler.

2. Propellant Combustion Product Analysis on an M16 Rifle and a 105 mm Caliber Gun, P. Ase, W. Eisenberg, S. Gordon, K. Taylor, and A. Snelson, J. Environ. Sci. Health, A20(3), 337 (1985).

3. U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes". U.S. EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. EPA-600/4-79-020 (1979).

4. As in 3 above.

5. B. M. Kneebone and H. Freiser, Determination Of Nitrogen Oxides in Ambient Air Using a Coated-Wire Nitrate Ion Selective Electrode, Analytical Chemistry, 45, 449, 1973.

6. NIOSH Manual of Analytical Methods, 2nd Edit. Method S308, U.S. Department of Health, Education and Welfare, 1978.

7. J. E. Bumgarner, "Standard Operating Procedures for the Preparation of Clean Tenax Cartridges". EMSL-SOP-EMD-013, U.S. EPA Environmental Monitoring Systems Laboratory, Research Triangle park, NC.

APPENDIX I

DETAILED PROCEDURES FOR HCN, NH_3, H_2S AND METAL PARTICULATE ANALYSES

CYANIDE ANALYTICAL PROCEDURE

2.1 Analysis of Aqueous Samples for Cyanide

Analytical Procedure: available
Sample Preparation: available

2.1.1 Reference

U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes." U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. EPA 600/4-79-020. (1979).

2.1.2 Method Summary

The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver-sensitive indicator.

2.1.3 Applicability

This method is applicable to most types of samples. The range can be easily adjusted by modifying the sample size subjected to distillation.

The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/l (0.25 mg/150 ml of absorbing liquid). The colorimetric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to abour 0.02 mg/l.

This method should be used to confirm and quantify the presence of cyanide after the hazardous waste screening procedure in Chapter II has produced a positive cyanide result.

2.1.4 Precision and Accuracy

In a single laboratory, using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/l CN,

the standard deviations were ±0.005, ±0.007, ±0.031 and ±0.094, respectively.

In a single laboratory, using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/l CN, recoveries were 85 and 102 percent, respectively.

2.1.5 Distillation

Place an aliquot of the sample, as appropriate, in the boiling flask of the distillation apparatus.

a. Place 500 ml of liquid sample, or an aliquot diluted to 500 ml, in the 1-liter boiling flask.

b. Place 5 to 50 g of soil or sediment in the boiling flask. Add 500 ml distilled water.

Add 50 ml sodium hydroxide solution (Subsection F 1.) to the absorbing tube and dilute, if necessary, with distilled water to obtain an adequate depth of liquid in the absorber tube. Connect the boiling flask, condenser, absorber, and trap in the train.

Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

Slowly add 25 ml conc. sulfuric acid (Subsection F.5.) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 ml of magnesium chloride solution into the air inlet and wash down with a stream of water. Heat the solution to boiling, taking care to prevent the solution from backing up into and over-flowing from the air inlet tube. Reflux for 1 hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

Drain the solution from the absorber into a 250-ml volumetric flask and bring up to volume with distilled water washings from the absorber tube.

Withdraw 50 ml or less of the solution from the flask and transfer to a 100-ml volumetric flask. If less than 50 ml is taken, dilute

to 50 ml with 0.25 N sodium hydroxide solution (Subsection F.4.). Add 15.0 ml sodium phosphate solution (Subsection F.6.) and mix.

2.1.6 Standard Preparation

Prepare a series of standards by pipeting suitable volumes of standard solution into 250-ml volumetric flasks. To each standard add 50 ml 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Prepare as follows:

ML of Standard Solution (1.0 = 5 µg CN)	Conc. mg CN per 250 ml
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	75
20.0	100

It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (one high and one low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards the operator should find the cause of the apparent error before proceeding.

2.1.7 Sample Analysis

The digests can be analyzed for cyanide either colorimetrically (paragraph 2.1.7.1) or by silver nitrate titration (paragraph 2.1.7.2).

2.1.7.1 Colorimetric Analysis

Transfer 50 ml of sample or cyanide standard, or an aliquot diluted to 50 ml with 0.25 N sodium hydroxide, to a 100-ml volumetric flask. Proceed with either paragraph (a.) or paragraph (b.).

a. Add 2 ml chloramine-T solution (Subsection F.12.) and mix. After 1 to 2 minutes, add 5 ml pyridine-barbituric acid solution (Subsection 13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1-cm cell within 15 minutes.

b. Add 0.5 ml chloramine-T and mix. After 1 to 2 minutes, add 5 ml pyridine-pyrazolone solution (Subsection 13.2) and mix. Dilute to volume with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1-cm cell.

NOTE: An excess of chloramine-T above 0.5 ml will inhibit color development with pyridine-pyrazolone.

Compare the sample absorbance to the calibration curve prepared from the cyanide standard absorbances in order to quantiby the cyanide in the samples.

2.1.7.2 Titration Analysis

Alternatively, if the sample contains more than 1 mg of CN, transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500-ml Erlenmeyer flask. Add 10 to 12 drops of the benzal-rhodanine indicator. 1

Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-ml microburet may be conveniently used to obtain a more precise titration.

I. CALCULATIONS

1. Liquid Samples

1.1 If the colorimetric procedure is used, calculate the cyanide concentration of the samples as follows:

$$CN, \mu g/l = \frac{A \times 1{,}000 \times 50}{B \quad C}$$

where:

A = µg CN read from standard curve 1.

B = ml of original sample for distillation

C = ml taken for colorimetric analysis.

1.2 If the titrimetric procedure is used, calculate the cyanide concentration of the samples as follows:

$$\text{CN, mg/l} = \frac{(X - D)\ 1{,}000}{\text{ml orig. sample}} \times \frac{250}{\text{ml of aliquot titrated}}$$

where:

X = volume of $AgNO_3$ for titration of sample

D = volume of $AgNO_3$ for titration of blank.

1. Solid-Phase Samples

Calculate the cyanide concentration of solid-phase samples as follows:

$$\text{CN µg/kg (wet weight)} = \frac{(A)(V)\ 1000}{g}$$

$$\text{CN µg/kg (dry weight)} = \frac{(A)(V)\ 1000}{(g)\ (\%S)}$$

where:

A = cyanide concentration in sample distillate, µg/l

V = final volume of sample distillate, l

g = wet weight of sample analyzed, g

%S = percent solids of sample as a decimal fraction.

REFERENCE

1. U.S. Environmental Protection Agency. "Methods for Chemical Analysis of Water and Wastes." U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. EPA-600/4-79-020. 1979.

AMMONIA ANALYTICAL PROCEDURE

METHODS FOR THE DETERMINATION OF AMMONIA

A. SCOPE

Analytical procedures presented in this Section are suitable for the determination of ammonia in aqueous samples and distillates and in extracts from other sample types. Colorimetric methods suitable for use in the low-µg/l range and a titrimetric method for samples in the mg/l range are presented.

B. SAMPLE HANDLING AND STORAGE

A flow diagram summarizing the pertinent information regarding sample handling and storage[1,2] is presented in Figure 1. Samples may be collected and stored in either glass or plastic containers. They should be analyzed as soon as possible and preferably within 24 hours.[1,3] Sample stability can be improved by adding sulfuric acid, tightly capping the sample bottle, and storing at 4°C until analyzed. The volume of sample required will vary from 20 to 25 ml for the automated procedures to 500 ml for a manual procedure.

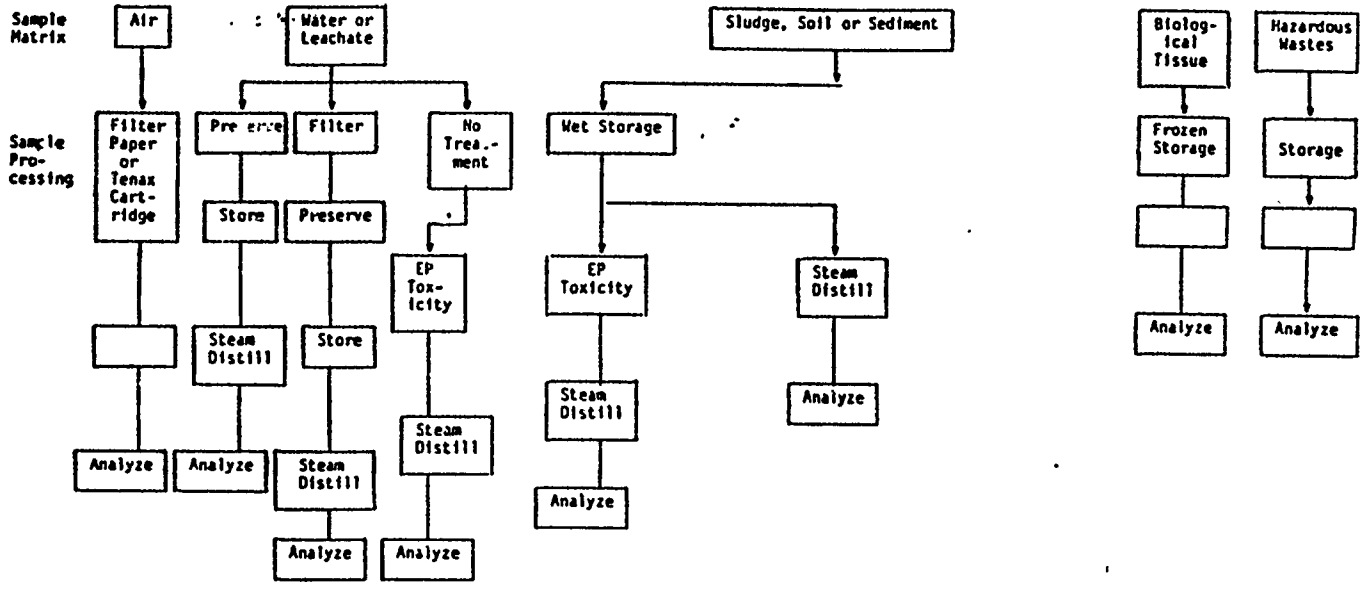
Sediment samples should be stored at 4°C in a field-moist condition. Drying or freezing of samples is not recommended because of the potential loss of ammonia during the drying, freezing or thawing cycles. The required sample size is 0.5 to 20 g.

C. INTERFERENCES

Calcium and magnesium ions may be present in sufficient concentration to cause precipitation problems during automated phenate analysis. A 5-percent EDTA solution is used to prevent the precipitation of calcium and magnesium ions from aqueous samples. For sea water samples, a sodium potassium tartrate solution is used.

Sample turbidity may interfere with the automated phenate method and must be removed by filtration prior to analysis. Sample color that absorbs light in the 630 to 660 nm photometric range will also interfere.

Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out some volatile compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.



Purpose	Total Conc. in Water	Soluble Conc. in Water	Mobility at pH 5	Mobility at pH 5	Total Conc. in Sediment	Total Conc. in Tissue	Total Conc. in Waste
Sample Container P	G, P	G, P	G, P	G, P	G, P		
Sample Preservative	H_2SO_4 pH<2 4°C	H_2SO_4 pH<2 4°C	4°C	4°C	4°C		
Storage Time		24hr	24hr	<1 w	<1 w		
Sample Size	40 ml	20-500 ml	20-500 ml		0.1-0.5 g		

Figure 1. Sample handling and storage for ammonia analysis.

A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent. When these samples are encountered, they must be distilled off prior to analysis.

Residual chlorine will react rapidly with ammonia. When chlorine is present or suspected of being present, the sample should be treated with sodium thiosulfate prior to distillation in order to remove the chlorine.

D. APPARATUS

1. Technicon Auto Analyzer Unit (AAI or AAII) consisting of:

   a. Sampler.

   b. Manifold (AAI) or analytical cartridge (AAII).

   c. Proportioning pump.

   d. Heating bath with double delay coil (AAI) (Subsection G.2.1).

   e. Dialyzer (Subsection G.2.2).

   f. Heating bath, 40°C (Subsection G.2.2).

   g. Colorimeter equipped with 15-mm tubular flow cell and 630- to 660-nm filters (Subsection G.2.1).

   h. Colorimeter equipped with a 50-mm flow cell and 420-nm filter (Subsection G.2.2).

   i. Recorder.

   j. Range expander.

   k. Digital printer for AAII (optional).

2. An all-glass distilling apparatus with an 800- to 1,000-ml flask.

3. Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

4. Nessler tubes: matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ± 1.5 mm inside measurement from bottom.

5. Erlenmeyer flasks: the distillate is collected in 500-ml glass-stoppered flasks. These flasks should be marked at the 350- and the 500-ml volume levels.

   With such marking it is not necessary to transfer the distillate to volumetric flasks.

6. Sampling train consisting of 4 impingers, a rotameter and a vacuum pump (Subsection G.2.5).

E. REAGENTS

1. Distilled water: special precaution must be taken to ensure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the the manufacturer's instructions.

   NOTE: All solutions must be made using ammonia-free water.

2. Sulfuric acid 5 N (air scrubber solution): carefully add 139 ml conc. sulfuric acid to approximately 500 ml ammonia-free distilled water. Cool to room temperature and dilute to 1 liter with ammonia-free distilled water.

3. Sodium phenolate: using a 1-liter Erlenmeyer flask, dissolve 83 g phenol in 500 ml distilled water. In small increments, cautiously add, with agitation, 32 g NaOH. Periodically cool the flask under a water faucet. When cool, dilute to 1 liter with distilled water.

4. Sodium hypochlorite solution: dilute 250 ml of a bleach solution containing 5.25 percent NaOCl (such as Clorox) to 500 ml with distilled water. Available chlorine level should approximate 2 to 3 percent. Since Clorox is a proprietary product, its formulation is subject to change. The analyst must remain alert to detect any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.

5. Sodium ethylenediamine-tetraacetate (EDTA) (5 percent): dissolve 50 g EDTA (disodium salt) and approximately six pellets of NaOH in 1 liter distilled water.

   NOTE: On saltwater samples where EDTA solution does not prevent precipitation of cations, sodium potassium tartrate solution may be used to advantage. It is prepared as follows:

6. Sodium potassium tartrate solution (10 percent $NaKC_4H_4O_6 \cdot 4\ H_2O$): to 900 ml distilled water, add 100 g sodium potassium tartrate. Add two pellets of NaOH and a few boiling chips; boil gently for 45 minutes. Cover, cool, and dilute to 1 liter with ammonia-free distilled water. Adjust pH to 5.2 ± 0.05 with H_2SO_4. After allowing to settle overnight in a cool place, filter to remove precipitate. Then add 0.5 ml Brij-35[8] (available from Technicon Corporation) solution and store in stoppered bottle.

7. Sodium nitroprusside (0.05 percent): dissolve 0.5 g sodium nitroprusside in 1 liter distilled water.

8. Stock solution: dissolve 3.819 g anhydrous ammonium chloride, NH_4Cl, dried at 105°C, in distilled water, and dilute to 1,000 ml. 1.0 ml = 1.0 mg NH_3-N.

9 Standard solution A: dilute 10.0 ml of stock solution to 1,000 ml with distilled water. 1.0 ml = 0.01 mg NH_3-N.

10. Standard solution B: dilute 10.0 ml of standard solution A to 100.0 ml with distilled water. 1.0 ml = 0.001 mg NH_3-N.

Working ammonia standards should be prepared fresh on the day of use. They can be prepared by diluting either standard solution A or standard solution B as indicated below:

NH_3-N, mg/l	ml Standard Solution/100 ml
	Solution B
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
	Solution A
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

When freshwater samples are being analyzed, the working ammonia standards should be diluted to volume with ammonia-free distilled water. When salt-water samples are being analyzed, the working ammonia standards should be diluted to volume with Substitute Ocean Water (SOW) that has the following composition:

Substitute Ocean Water (SOW)

NaCl	24.53 g/l	$NaHCO_3$	0.20 g/l
$MgCl_2$	5.20 g/l	KBr	0.10 g/l
Na_2SO_4	4.09 g/l	H_3BO_3	0.03 g/l
$CaCl_2$	1.16 g/l	$SrCl_2$	0.03 g/l
KCl	0.70 g/l	NaF	0.003 g/l

If SOW is used, subtract its blank background response from the standards before preparing the standard curve.

11. Alkaline complexing agent:

    Solution A: dissolve 52 g sodium hydroxide, NaOH, in 1 liter deionized water.

    Solution B: dissolve 40 g sodium hexametaphosphate in 1 liter deionized water.

    The alkaline complexing agent should be prepared fresh daily by mixing equal volumes of solution A and solution B (i.e. 100 ml A and 100 ml B).

12. Buffer: dissolve 96 g hydrated disodium hydrogen phosphate and 10 g sodium dihydrogen phosphate in 5 l deionized water (pH 7.5).

13. Sodium hypochlorite: dilute sodium hypochlorite solution (Clorox is suitable) to approximately 0.004 percent available chlorine with deionized water.

14. Oxalic acid: dissolve 20 g oxalic acid and 170 g monochloracetic acid in deionized water and make up to 1 liter.

15. Orthotolidine: prepare by heating 1.2 g O-tolidine dihydrochloride in 120 ml conc. hydrochloric acid, HCl, at 60°C for 1 hour; then adjust to a volume of 1 liter with distilled water.

16. Boric acid solution (20 g/): dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

17. Mixed indicator: mix two volumes of 0.2-percent methyl red in 95-percent ethyl alcohol with 1 volume of 0.2-percent methylene blue in 95-percent ethyl alcohol. This solution should be prepared fresh every 30 days.

    NOTE: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95-percent ethanol.

18. Nessler reagent: dissolve 100 g mercuric iodide and 70 g potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 ml water. Dilute the mixture to 1 l. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

    NOTE: This reagent should give the characteristic color with ammonia within 10 minutes after addition and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50-ml volume).

19. Borate buffer: add 88 ml of 0.1 N NaOH solution to 500 ml 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10\ H_2O$ per liter) and dilute to 1 liter.

20. Sulfuric acid, standard solution (0.02 N, 1 ml = 0.28 mg NH_3-N): prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water.

NOTE: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution, the 0.02 N acid can then be prepared. Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1,000 ml with CO_2-free distilled water.

21. Sodium hydroxide, 1 N: dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

22. Dechlorinating reagents: a number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

    a. Sodium thiosulfate (0.0142 N): dissolve 3.5 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter. One milliliter of this solution will remove 1 mg/liter of residual chlorine in 500 ml of sample.

    b. Sodium arsenite (0.0142 N): dissolve 1.0 g $NaAsO_2$ in distilled water and dilute to 1 liter.

23. Silica Gel.

24. Sodium phosphate buffer (11% w/v): dissolve 11 g trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, in 100 ml ammonia-free distilled water.

25. Phenate reagent: dissolve 340 g phenol in 500 ml of absolute methanol. Dissolve 0.1 g sodium nitroprusside in 15 ml ammonia-free distilled water, add 75 ml of phenol solution and dilute the solution to 100 ml with ammonia-free distilled water.

26. Sodium hydroxide solution (5M): dissolve 20 g sodium hydroxide in 100 ml ammonia-free distilled water.

27. Basic sodium hypochlorite solution: mix 11.5 ml commercial bleach (2.5% Cl) and 20 ml 5M NaOH in a 100-ml volumetric flask and dilute to volume with ammonia-free distilled water.

F. QUALITY CONTROL

The following quality control elements should be incorporated into an analytical program for ammonia:

A reference standard should be routinely analyzed with samples to determine the accuracy of the method. A control limit of ±10 percent from the true value should be considered acceptable.

Duplicate samples should be run every tenth sample or with each sample set (whichever frequency is higher) to establish the precision of the method. A relative percent difference of 20 percent or less between duplicates is considered acceptable.

Spiked samples should be analyzed every tenth sample as a monitor of potential matrix effects. Spike recoveries should be within the 80- to 120-percent range.

2.1 Analysis for Ammonia in Aqueous Samples Using an Automated Phenate Procedure

Analytical Procedure: evaluated
Sample Preparation: evaluated

2.1.1 Reference

U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes." U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. EPA-600/4-79-020 (1979).[1]

American Public Health Association. "Standard Methods for the Examination of Water and Wastewater Including Bottom Sediments and Sludges." APHA, New York, New York. 1193 p. 15th Ed. (1980).[4]

2.1.2 Method Summary

The sample is allowed to react with alkaline phenol and hypochlorite to form indophenol blue that is proportional to the original ammonia concentration. The blue color that is formed is intensified with sodium nitroprusside and measured photometrically at 630 to 660 nm. Approximately 20 to 60 samples per hour can be analyzed with the automated method.

2.1.3 Applicability

This method covers the determination of ammonia in drinking, surface, and saline waters as well as domestic and industrial wastes when present within the concentration range of 0.01 to 2.0 mg/l NH_3 as N. Higher concentrations can be quantified after the appropriate sample dilution.

2.1.4 Precision and Accuracy

Using the automated phenate procedure with a Technicon AAI system in a single laboratory, surface water samples at concentrations of 1.41, 0.77, 0.59, and 0.43 mg NH_3-N/l, the standard deviation was ±0.005. Recoveries of ammonia at 0.16 and 1.44 mg NH_3-N/l were 107 and 99 percent, respectively.

2.1.5 Sample Analysis

Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the wash water and the standard ammonia solutions should be approximately that of the samples. For example, if the samples have been preserved with 2 ml conc. H_2SO_4/l, the wash water and standards should also contain 2 ml conc. H_2SO_4/l.

For a working range of 0.01 to 2.00 mg NH_3-N/l (AAI), set up the manifold as shown in Figure 2. For a working range of 0.01 to 1.0 mg NH_3-N/l (AAII), set up the manifold as shown in Figure 3.

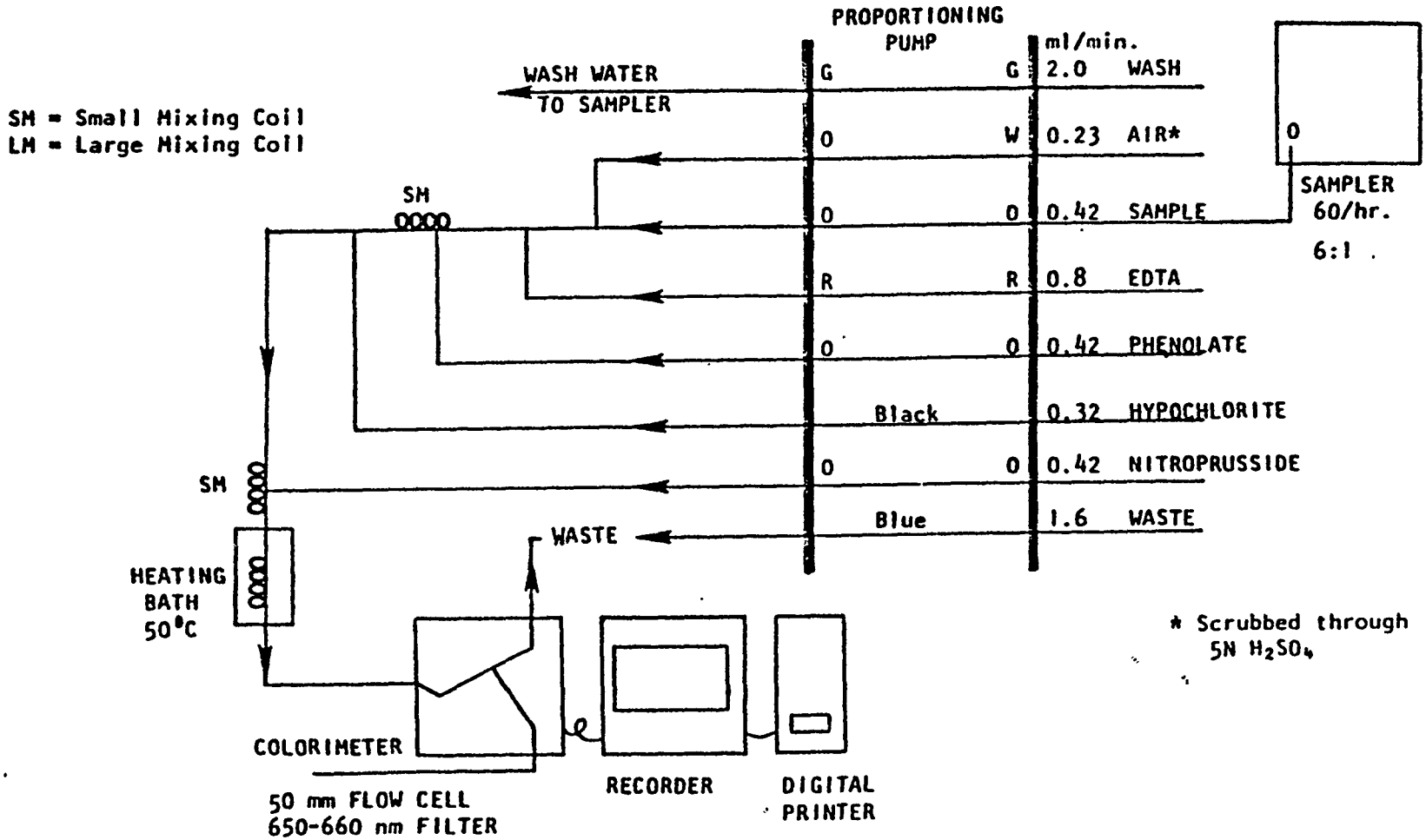


Figure 2. AAI manifold for phenate determination of ammonia.

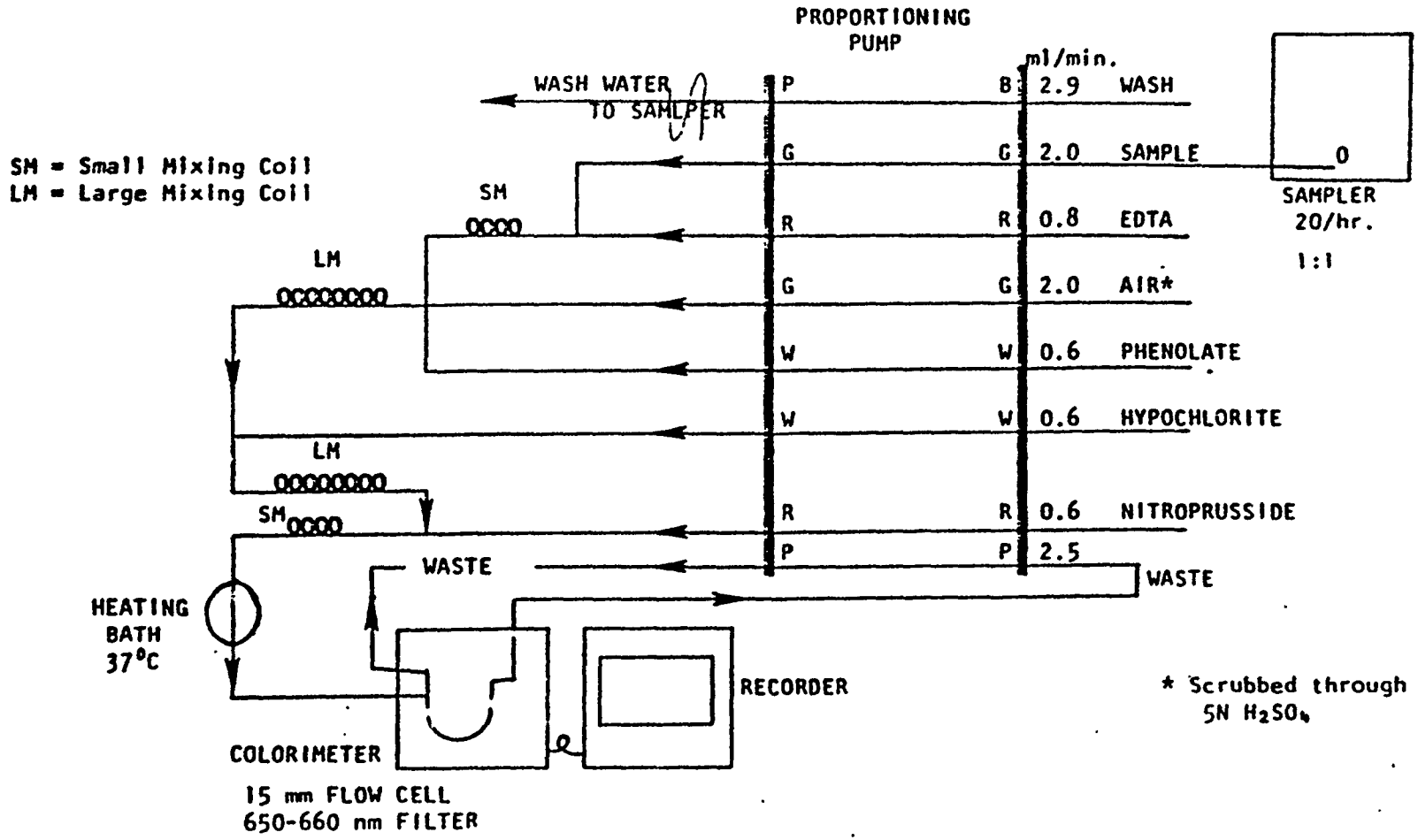


Figure 3. AAII cartridge for phenate determination of ammonia.

Higher concentrations may be accommodated by sample dilution. Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents while feeding distilled water through the sample line.

For the AAI system, sample at a rate of 20/hour (a 1:1 cam). For the AAII, use a 60/hour, 6:1 cam with a common wash.

Arrange ammonia standards in the sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

Switch sample line from distilled water to sampler and begin processing samples.

HYDROGEN SULFIDE ANALYTICAL PROCEDURE

Hydrogen Sulfide

NIOSH Manual of Analytical Methods

Analyte:	Hydrogen Sulfide	Method No.: S4
Matrix:	Air	Range: 8.5-63 mg/cu m
OSHA Standard:	20 ppm (30 mg/cu m) - Ceiling 50 ppm (70 mg/cu m) - Peak	Precision ($\overline{CV}_T$): 0.121
Procedure:	Absorption - Methylene Blue Spectrophotometric	Validation Date: 9/13/74

1. Principle of the Method

1.1 Hydrogen sulfide is collected by aspirating a measured volume of air through an alkaline suspension of cadmium hydroxide (Reference 11.1). The sulfide is precipitated as cadmium sulfide to prevent air oxidation of the sulfide which occurs rapidly in an aqueous alkaline solution. STRactan 10® is added to the cadmium hydroxide slurry to minimize photo-decomposition of the precipitated cadmium sulfide (Reference 11.2). The collected sulfide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with an acid solution of N,N-dimethyl-p-phenylenediamine and ferric chloride (References 11.3, 11.4, 11.5).

1.2 Collection efficiency is variable below 10 µg/cu m and is affected by the type of scrubber, the size of the gas bubbles, and the contact time with the absorbing solution and the concentration of hydrogen sulfide (References 11.6, 11.7, 11.8).

2. Range and Sensitivity

2.1 This method was validated over the range of 8.5-63 mg/cu m at an atmospheric temperature and pressure of 25°C and 760 mm Hg, using a 2 liter sample. Under the conditions of sample size (2 liters) the probable useful range of the method is 5-100 mg/cu m. For sample concentrations outside this range the sampling volume should be modified.

3. Interferences

3.1 The methylene blue reaction is highly specific for sulfide at the low concentrations usually encountered in ambient air. Strong

reducing agents (e.g. SO_2) inhibit color development. Even sulfide solutions containing several micrograms sulfite per ml show this effect and must be diluted to eliminate color inhibition. If sulfur dioxide is absorbed to give a sulfite concentration in excess of 10 µg/ml color formation is retarded. The use of 0.5 ml of ferric chloride solution during analysis eliminates the SO_2 interference up to 40 µg/ml.

3.2 Nitrogen dioxide gives a pale yellow color with the sulfide reagents at 0.5 µg/ml or more. No interference is encountered when 0.3 ppm NO_2 is aspirated through a midget impinger containing a slurry of cadmium hydroxide-cadmium sulfide-STRactan 10®. If H_2S and NO_2 are simultaneously aspirated through cadmium hydroxide-STRactan 10® slurry, lower H_2S results are obtained, probably because of gas phase oxidation of the H_2S prior to precipitation as CdS (Reference 11.8).

3.3 Ozone at 57 ppb reduced the recovery of sulfide previously precipitated as CdS by 15 per cent (Reference 11.8).

3.4 Substitution of other cation precipitants for the cadmium in the absorbent (i.e. zinc, mercury, etc.) will shift or eliminate the absorbance maximum of the solution upon addition of the acid-amine reagent.

3.5 Cadmium sulfide decomposes significantly when exposed to light unless protected by the addition of 1 per cent STRactan® to the absorbing solution prior to sampling (Reference 11.2).

3.6 The choice of impinger used to trap H_2S with the $Cd(OH)_2$ slurry is very important when measuring concentration in the range 5-100 mg/cu m. Impingers or bubblers having fritted-end gas delivery tubes are a problem source if the sulfide in solution is oxidized to free sulfur by oxygen from the atmosphere. The sulfur collects on the fritted glass membrane and may significantly change the flow rate of the air sample through the system. One way of avoiding this problem is to use a midget impinger with standard glass-tapered tips.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.5-63 mg/cu m was 0.121. This value corresponds to a 3.6 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.9.

4.2 On the average the values obtained using the overall sampling and analytical method were 10% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 Effect of Light and Storage - Disadvantage

5.1.1 Hydrogen sulfide is readily volatilized from aqueous solution when the pH is below 7.0. Alkaline, aqueous sulfide solutions are very unstable, because sulfide ion is rapidly oxidized by exposure to the air.

5.1.2 Cadmium sulfide is not appreciably oxidized even when aspirated with pure oxygen in the dark. However, exposure of an impinger containing cadmium sulfide to laboratory or to more intense light sources produces an immediate and variable photo-decomposition. Losses of 50-90 per cent of added sulfide have been routinely reported by a number of laboratories. Even though the addition of STRactan 10® to the absorbing solution controls the photo-decomposition (Reference 11.2), it is necessary to protect the impinger from light at all times. This is achieved by the use of low actinic glass impingers, paint on the exterior of the impingers, or an aluminum foil wrapping.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:

6.1.1 A graduated 25-ml midget impinger with a standard glass-tapered gas delivery tube containing the absorbing solution or reagent. The impinger should be wrapped in aluminum foil to protect the sample from exposure to light.

6.1.2 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter or rotameter capable of measuring 2 liters of air at 0.2 liter per minute with an accuracy of ±5%. Instead of these, calibrated hypodermic needles may be used as critical orifices if the pump is capable of maintaining greater than 0.7 atmospheric pressure differential across the needle (Reference 11.10).

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Associated laboratory glassware.

6.3 Colorimeter with red filter or spectrophotometer at 670 nm.

6.4 Matched cells, 1-cm path length.

7. Reagents

All reagents must be ACS analytical reagent quality. Distilled water should conform to the ASTM Standards for Referee Reagent Water.

All reagents should be refrigerated when not in use.

7.1 Amine-sulfuric Acid Stock Solution. Add 50 ml concentrated sulfuric acid to 30 ml water and cool. Dissolve 12 g of N,N-dimethyl-p-phenylene-diamine dihydrochloride* (para-aminodimethylaniline) (redistilled if necessary) in the acid. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

7.2 Amine Test Solution. Dilute 25 ml of the Stock Solution to 1 liter with 1:1 sulfuric acid.

7.3 Ferric Chloride Solution. Dissolve 100 g of ferric chloride, $FeCl_3 \cdot 6H_2O$ in water and dilute to 100 ml.

7.4 Ethanol, 95%.

7.5 STRactan 10®. (Arabinogalactan) Available from Chicago Scientific, Inc., 716 W. Irving Park Road, Bensenville, IL 60106. Arabinogalacta sold under other brand names may be used.

7.6 Cadmium Sulfate-STRactan® Solution. Dissolve 8.6 g of $3CdSO_4 \cdot 8H_2O$ in approximately 600 ml of water. Add 20 g STRactan 10® and dilute to 1 liter.

7.7 Sodium Hydroxide Solution. Dissolve 0.6 g sodium hydroxide in approximately 600 ml of water and dilute to 1 liter.

7.8 Cadmium Hydroxide-STRactan® Absorbing Solution. This absorbing solution is prepared by pipeting 5 ml of cadmium sulfate-STRactan® solution (7.6) and 5 ml of sodium hydroxide solution (7.7) directly into the midget impinger and mixing. This solution is stable for 3 to 5 days.

7.9 Stock Sodium Sulfide Standard. Place 35.28 g of $Na_2S \cdot 9H_2O$ into a 1 liter volumetric flask and add enough oxygen free distilled water to bring the volume to 1 liter. Store under nitrogen and refrigerate. Standardize with standard iodine and thiosulfate solution in an iodine flask under a nitrogen atmosphere to minimize air oxidation. The approximate concentration of the sulfide solution will be 4700 µg sulfide/ml of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

* 10.5 g N,N-dimethyl-p-phenylenediamine oxalate may be used.

7.10 Working Sodium Sulfide Solution. Dilute 25 ml of stock solution (7.9) with oxygen free water to 250 ml. This solution contains the sulfide equivalent of approximately 500 μg/ml of H_2S. Make fresh working sulfide solution daily. The actual concentration of this solution can be determined from the titration results on the stock sodium sulfide standard (7.9).

For the most accurate results in the iodometric determination of sulfide in aqueous solution, the following general procedure is recommended:

1. Replace the oxygen from the flask by flushing with an inert gas such as carbon dioxide or nitrogen.

2. Add an excess of standard iodine, acidify, and back titrate with standard thiosulfate and starch indicator (Reference 11.14).

8. Procedure

8.1 Cleaning of Equipment. All glassware should be thoroughly cleaned; the following procedure is recommended:

8.1.1 Wash with a detergent and tap water solution followed by tap water and distilled water rinses.

8.1.2 Soak in 1:1 or concentrated nitric acid for 30 minutes and then follow with tap, distilled, and double distilled water rinses.

8.2 Collection and Shipping of Samples

8.2.1 Prepare 10 ml of absorbing solution as described in Section 7.8 directly in the midget impinger. The addition of 5 ml of 95% ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours (induced by the presence of STRactan 10®). In addition, 1 or 2 Teflon demister discs may be slipped up over the impinger air inlet tube to a height approximately 1 to 2" from the top of the tube. Wrap the impinger with aluminum foil.

8.2.2 Connect the impinger (via the absorption tube) to the sampling pump with a short piece of flexible tubing.

8.2.3 Air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.4 At the ceiling and peak concentrations, a sample size of 2 liters is recommended. Sample for 10 minutes at a flow of 0.20 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.2.5 Turn on the pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible.

8.2.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.

8.2.7 After sampling, the impinger stem must not be removed since it contains CdS deposits. It is necessary to ship the impingers with the stems in so the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e. taped) to secure the top tightly.

8.2.8 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.9 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.10 A "blank" impinger should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this impinger.

8.3 Analysis

8.3.1 Remove the impinger top and drain it thoroughly into the impinger bottom. Set aside. Transfer the solution and deposit in the impinger bottom to a 250-ml volumetric flask. Using 50 ml of distilled water rinse the bottom twice with the aid of a clean rubber policeman on a glass stirring rod. Add the rinse solutions to the volumetric flask. With the aid of the rubber policeman wash the outside of the impinger stem with 20 ml of distilled water and add the washings to the flask and drain 20 ml of distilled water through it into the flask. The total wash water volume should be 90 ml.

8.3.2 Add 15 ml of amine test solution through the impinger inlet tube into the volumetric flask. This is necessary to dissolve the CdS deposited inside the inlet tube. Mix gently to avoid loss of H_2S.

8.3.3 Add 0.5 ml of ferric chloride solution and mix. Bring to volume with distilled water. Allow to stand 20 minutes.

8.3.4 Prepare a zero reference solution in the same manner using a 10-ml volume of absorbing solution, through which no air has been aspirated.

8.3.5 Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100 per cent transmission against the zero reference.

9. Calibration and Standards

9.1 Aqueous Sulfide

9.1.1 Place 5 ml of each of the absorbing solutions (Sections 7.6 and 7.7) into each of a series of 250 ml volumetric flasks. Add standard sulfide solution equivalent to 0, 20, 40, 80, 120, 160 µg of hydrogen sulfide to the different flasks.

9.1.2 Add 90 ml of distilled water.

9.1.3 Add 15 ml of amine-acid test solution to each flask and mix gently.

9.1.4 Add 0.5 ml of ferric chloride solution to each flask. Mix, make up to volume, and allow to stand for 20 minutes.

9.1.5 Determine the absorbance in a spectrophotometer at 670 nm against the sulfide-free reference solution.

9.1.6 Prepare a standard curve of absorbance versus µg H_2S.

9.2 Gaseous Sulfide. Cylinders of hydrogen sulfide in dry nitrogen in the range desired are available commercially, and may be used to prepare calibration curves for use at the 10-60 mg/cu m levels. Nitrogen containing hydrogen sulfide in the 450-600 mg/cu m range can be diluted to the desired concentrations. Analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide.

9.2.1 Prepare or obtain a cylinder of nitrogen containing hydrogen sulfide in the range of 450-600 mg/cu m.

9.2.2 To obtain standard concentrations of hydrogen sulfide, assemble the apparatus consisting of appropriate pressure regulators, needle valves and flow meters for the nitrogen and for a dry air diluent stream. All stainless steel, glass or rubber tubing must be used for the hydrogen sulfide mixture. Flow of hydrogen sulfide in nitrogen is controlled by a needle valve operated in conjunction with a previously calibrated flow meter in the range of 0.2 to 2.0 liters per minute. Diluent dry air from a cylinder is controlled by a similar needle valve-flow meter combination in the range of 1 to 20 liters per minute. The hydrogen sulfide in nitrogen and the diluent air are combined in a mixing chamber at atmospheric

pressure, from which they flow through a baffle tube in which mixing takes place into a 1 liter sampling flask which is provided with one or more nipples from which samples can be taken. Sampling is done by connecting a midget impinger to the nipple and drawing a known volume of the mixture through the impinger for a measured length of time, using a critical orifice to control flow at a constant known rate.

9.2.3 Procedure for Preparing Simulated Calibration Curves. The following description represents a typical procedure for air sampling of short duration.

1. The system is designed to provide an accurate measure of hydrogen sulfide in the 10-60 mg/cu m range. It can be easily modified to meet special needs.

2. The dynamic range of the colorimetric procedure fixes the total volume of the sample at 2 liters; then, to obtain linearity between the absorbance of the solution and the concentration of hydrogen sulfide in mg/cu m, select a constant sampling time. This fixing of the sampling time is desirable also from a practical standpoint. In this case, select a sampling time of 10 minutes. To obtain a 2 liter sample of air requires a flow rate of 0.2 liter per minute. The concentration of standard H_2S in air is computed as follows:

$$C = \frac{cf}{F + f}$$

where:

C = concentration of H_2S in mg/cu m

c = concentration of H_2S in nitrogen, before dilution

F = flow of diluent air, as measured by calibrated flow meter

f = flow of H_2S in nitrogen, as measured by calibrated flow meter.

9.2.4 Commercially prepared hydrogen sulfide in nitrogen can be obtained with a known concentration, as analyzed by the laboratory preparing the gas. If it is desired to check this concentration, measured volume of the gas can be bubbled through the absorbing solutions, and the collected sulfide titrated against iodine-thiosulfate. The volume of gas can be measured using a wet test meter.

9.2.5 If hydrogen sulfide is present at much lower concentrations (1.5 to 140 μg/cu m), commercially available permeation tubes containing liquified hydrogen sulfide may be used to prepare calibration tubes (Reference 11.8, 11.11, 11.12, 11.13, 11.14).

10. Calculations

10.1 Gaseous Sulfide

10.1.1 Using the Beers-Law Standard curve of absorbance versus μg H_2S determine μg H_2S in the sampling impinger corresponding to its absorbance reading at 670 nm.

10.1.2 The concentration of H_2S in the air sampled can be expressed in mg/cu m which is numerically equal to μg/liter.

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\mu\text{g } H_2S \text{ (Section 10.1)}}{\text{Air volume sampled (liter)}}$$

10.1.3 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

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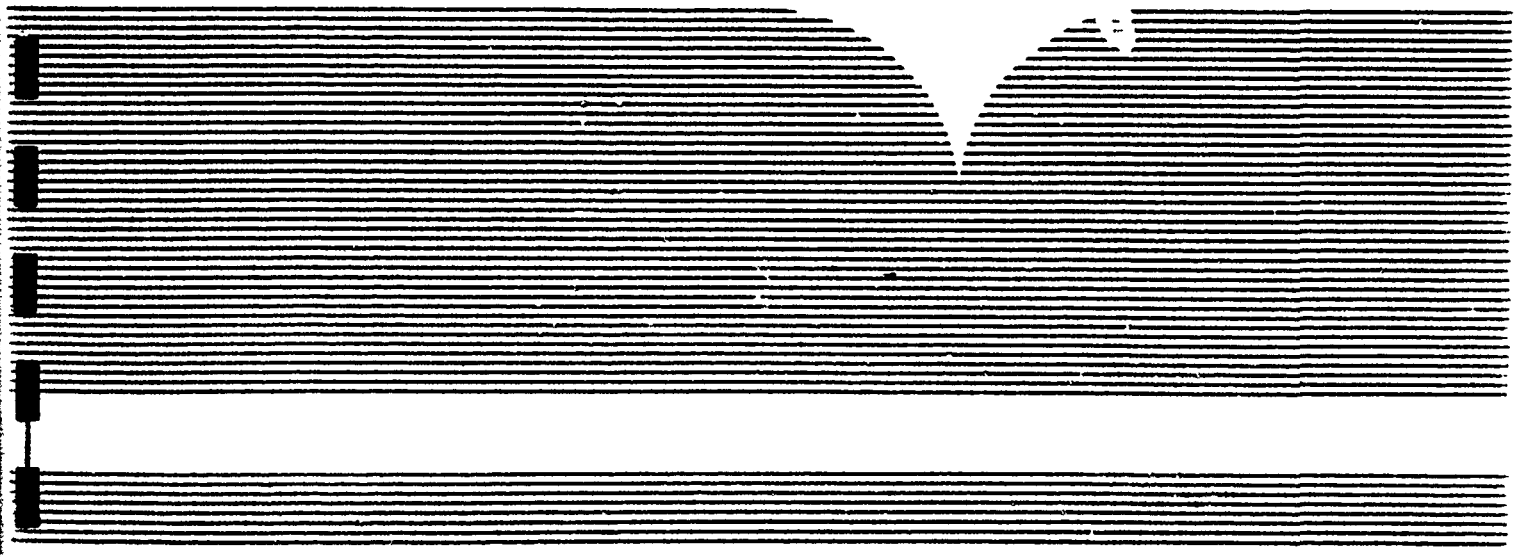
METAL PARTICULATE ANALYTICAL PROCEDURES

PB84-191048

CHARACTERIZATION OF HAZARDOUS WASTE SITES, A METHODS MANUAL. VOLUME III. AVAILABLE LABORATORY ANALYTICAL METHODS

Lockheed Engineering Management Services Company
Las Vegas, NV

May 84



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

SECTION 15

METHODS FOR THE DETERMINATION OF TRACE METALS USING INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

A. SCOPE

This method may be used for the simultaneous multi-element determination of metals in aqueous samples and some types of hazardous wastes.[1] Care must be exercised to ensure that samples and standards are corrected for any matrix differences in order to correct for potential interferences. Actual working detection limits for the method are dependent on the sample matrix and the method of sample preparation.

B. SAMPLE HANDLING AND STORAGE

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus, the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water, rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (see NOTES 1 and 2).

NOTE 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove residual traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, New York 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 2: If it can be documented through an active analytical quality control progam using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

Before collection of the sample, a decision must be made as to the type of data desired (dissolved, suspended, or total concentration) so that the appropriate preservation and pretreatment steps may be accomplished.

Filtration and acid preservation are to be performed at the time the sample is collected or as soon as possible thereafter.

For the determination of dissolved elements the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50 to 100 ml of sample to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 ml of (1+1) acid per liter should be sufficient to preserve the sample. Recommended storage time for samples preserved in this manner is 90 days (Figure 1).[2]

For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

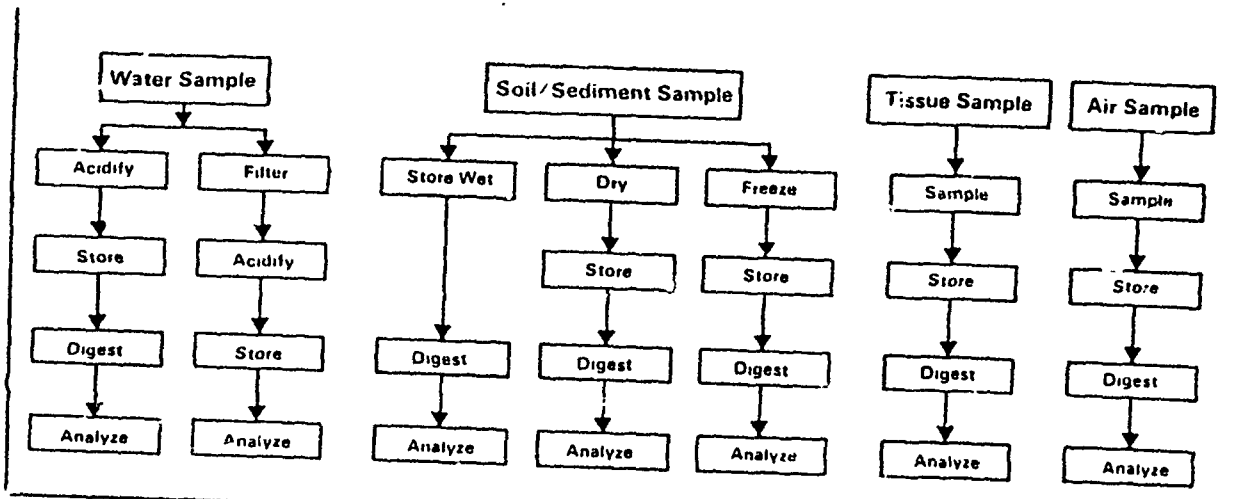
For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing. Either glass or plastic containers may be used. The recommended holding time is 90 days.[2]

Storage and sample handling information for soil and sediment samples is also presented in Figure 1. There are no known effective chemical preservatives and the maximum storage time is unknown. This information is also unknown for hazardous waste samples.

C. INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:[1]

1. Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high-concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effect can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 1 are some interference effects for the recommended wavelengths. The data in Table 1 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferences can be assumed.



Purpose	Total Water Concentration	Soluble Water Concentration	Total Sediment Concentration	Total Sediment Concentration	Total Sediment Concentration	Total Particulate Concentration
Container	G, P	G, P	G, P	G, P	G, P	Glass Fiber Membrane Filter
Sample Treatment	None	Filter	None	Air Dry	Freeze	None
Preservative	HNO_3 pH<2	HNO_3 pH<2	4°C	None	None	None
Storage Time	90d	90d	1w			indefinite
Digestion Solution	Strong Acid	None	Strong Acid	Strong Acid	Strong Acid	Strong Acid
Sample Amount	100-500 ml	100-500 ml	2-5 g	2-5 g	2-5 g	2000 m³

Figure 1. Handling and sample storage information for metals analysis.

TABLE 1. ANALYTE CONCENTRATION EQUIVALENTS (mg/l) ARISING FROM INTERFERENT AT THE 100 mg/l LEVEL[1]

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

The interference information, which was collected at the Ames Laboratory*, is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/l of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/l of aluminum. According to Table 1, 100 mg/l of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/l. Therefore, 10 mg/l of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/l. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 1, and that the interference effects must be evaluated for each individual system.

Only those interferences listed were investigated and the blank spaces in Table 1 indicate that measurable interferences were not observed for the interferent concentrations used. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2 to 5 percent of the peaks generated by the analyte concentrations.

At present, information on the primary silver and potassium wavelengths is not available but it has been reported that second-order energy from the magnesium 383.231 nm wavelength interferes with the potassium line at 766.491 nm.[1]

2. Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples that contain high dissolved solids concentrations or are characterized by extreme pH values. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem that can occur when analyzing samples with high dissolved solids concentrations is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate with the use of mass flow controllers improves instrument performance.

3. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique. However, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration

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data for analyte elements. These tests, as outlined below, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

Serial dilution. If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

Spike addition. The recovery of a spike added to the sample at a minimum level of 10X the instrumental detection limit (maximum 100X) should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

Caution: The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

Comparison with alternate method of analysis. When investigating a new sample matrix, comparison tests should be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

Wavelength scanning of analyte line region. If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

D. APPARATUS

1. Inductively coupled plasma-atomic emission spectrometer.

2. Computer-controlled atomic emission spectrometer with background correction.

3. Radiofrequency generator.

4. Argon gas supply, welding grade or better.

Operating conditions. Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating

conditions used satisfy the analytical requirements. Quality control data should be maintained to confirm instrument performance and analytical results.

5. Compact box furnace, temperature controlled.

6. Exhaust hood or suitable venting system.

7. Disposable graphite crucibles (SPEX 7152).

8. Polyethylene vials, 8 ml, capped.

9. Cinder plate (or suitable heat-proof material).

10. Vacuum desiccator.

11. Analytical balance.

12. Weighing dishes.

13. Tongs.

E. REAGENTS

1. Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

   Acetic acid, conc. (sp. gr. 1.06).

   Hydrochloric acid, conc. (sp. gr. 1.19).

   Hydrochloric acid, (1+1): Add 500 ml conc. HCl (sp. gr. 1.19) to 400 ml deionized, distilled water and dilute to 1 liter.

   Nitric acid, conc. (sp. gr. 1.41).

   Nitric acid, (1+1): Add 500 ml conc. HNO_3 (sp. gr. 1.41) to 400 ml deionized, distilled water and dilute to 1 liter.

2. Deionized, distilled water. Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards, and as dilution water.

3. Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 hour at 105°C unless otherwise specified.

   3.1 Aluminum solution, stock, 1 ml = 100 µg Al: dissolve 0.100 g aluminum metal in an acid mixture of 4 ml (1+1) HCl and 1 ml conc. HNO_3 in a beaker. Warm gently to effect solution. When

solution is complete, transfer quantitatively to a 1-l flask, add an additional 10 ml of (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

3.2 Antimony solution, stock, 1 ml = 100 µg Sb: dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized, distilled water, add 10 ml (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

3.3 Arsenic solution, stock, 1 ml = 100 µg As: dissolve 0.1320 g As_2O_3 in 100 ml deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.4 Barium solution, stock, 1 ml = 100 µg Ba: dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hours) in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

3.5 Beryllium solution, stock, 1 ml = 100 µg Be: dissolve 1.966 g $BeSO_4 \cdot 4H_2O$ (do not dry), in deionized, distilled water, add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.6 Boron solution, stock, 1 ml = 100 µg B: dissolve 0.5716 g anhydrous H_3BO_3 (do not dry) in deionized, distilled water and dilute to 1,000 ml. Keep the bottle tightly stoppered, and store in a desiccator.

3.7 Cadmium solution, stock, 1 ml = 100 µg Cd: dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.8 Calcium solution, stock, 1 ml = 100 µg Ca: suspend 0.2498 g $CaCO_3$, dried at 180°C for 1 hour before weighing, in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.9 Chromium solution, stock, 1 ml = 100 µg Cr: dissolve 0.1923 g CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.10 Cobalt solution, stock, 1 ml = 100 µg Co: dissolve 0.1000 g cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 ml (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

3.11 Copper solution, stock, 1 ml = 100 µg Cu: dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.12 Iron solution, stock, 1 ml = 100 µg Fe: dissolve 0.1430 g Fe_2O_3 in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.13 Lead solution, stock, 1 ml = 100 µg Pb: dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.14 Magnesium solution, stock, 1 ml = 100 µg Mg: dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.15 Manganese solution, stock, 1 ml = 100 µg Mn: dissolve 0.1000 g manganese metal in an acid mixture consisting of 10 ml conc. HCl and 1 ml conc. HNO_3, and dilute to 1,000 ml with deionized, distilled water.

3.16 Molybdenum solution, stock, 1 ml = 100 µg Mo: dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 ml.

3.17 Nickel solution, stock, 1 ml = 100 µg Ni: dissolve 0.1000 g nickel metal in 10 ml hot conc. HNO_3, cool, and dilute to 1,000 ml with deionized, distilled water.

3.18 Potassium solution, stock, 1 ml = 100 µg K: dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water and dilute to 1,000 ml.

3.19 Selenium solution, stock, 1 ml = 100 µg Se: dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) (do not dry) in deionized, distilled water and dilute to 1,000 ml.

3.20 Silica solution, stock, 1 ml = 100 µg SiO2: dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ (do not dry) in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.21 Silver solution, stock, 1 ml = 100 µg Ag: dissolve 0.1575 g $AgNO_3$ in 100 ml deionized, distilled water and 10 ml conc. HNO_3. Dilute to 1,000 ml with deionized, distilled water.

3.22 Sodium solution, stock, 1 ml = 100 µg Na. dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.23 Thallium solution, stock, 1 ml = 100 µg Tl: dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.24 Vanadium solution, stock, 1 ml = 100 µg V: dissolve 0.2297 g NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

3.25 Zinc solution, stock, 1 ml = 100 µg Zn: dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

4. Mixed calibration standard solutions. Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add 2 ml (1+1) HNO_3 and 10 ml (1+1) HCl and dilute to 100 ml with deionized, distilled water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability. Some typical calibration standard combinations are suggested below.

4.1 Mixed standard solution I: Manganese, beryllium, cadmium, lead, and zinc.

4.2 Mixed standard solution II: Barium, copper, iron, vanadium, and cobalt.

4.3 Mixed standard solution III: Molybdenum, silica, arsenic, and selenium.

4.4 Mixed standard solution IV: Calcium, sodium, potassium, aluminum, chromium, and nickel.

4.5 Mixed standard solution V: Antimony, boron, magnesium, silver, and thallium. NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 ml of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 ml with deionized, distilled water. For this acid combination, the silver concentration should be limited to 2 mg/l. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

5. Two types of blanks are required. The calibration blank is used in establishing the analytical curve while the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.1 The calibration blank is prepared by diluting 2 ml (1+1) HNO_3 and 10 ml (1+1) HCl to 100 ml with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6. In addition to the calibration standards, an instrument check standard, an interference check sample, and a quality control sample must be analyzed with each set of samples.

6.1 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves.

6.2 The interference check sample. Select a representative sample which contains minimal concentrations of the analytes of interest but a known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 µg/l or 5 times the estimated detection limits. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the types of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample is available from the Quality Assurance Branch, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

6.3 The quality control sample should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/l and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured.

7. $LiBO_2$, anhydrous (G. F. Smith No. 304).

8. LiF, powder (Alfa No. 87628).

9. P_2O_5.

10. Indicating $CaSO_4$.

F. QUALITY CONTROL

1. Check the instrument standardization by analyzing appropriate quality control check standards as follows:

1.1 Analyze an appropriate instrument check standard (Subsection E.6.1) containing the elements of interest at a frequency of 10 percent. This check standard is used to determine instrument drift. If agreement is not within ±10 percent of the expected values or within the established control limits, whichever is lower, the analysis should be considered out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (Subsection E.5.1) at a frequency of 10 percent. The result should be within the established control limits of 2 standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

1.2 To verify interelement and background correction factors analyze the interference check sample (Subsection E.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

1.3 A quality control sample (Subsection E.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within ±5 percent of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

G. ANALYTICAL PROCEDURES

1.1 ICAP Determination of Metals in LMB/LiF Fusion Pellets of Waste Samples

Analytical Procedure: available
Sample Preparation: available

1.1.1 Reference

U.S. Environmental Protection Agency, "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Elemental Analysis of Prepared Hazardous Waste Samples." U.S. EPA, National Enforcement Investigation Center, Denver, Colorado. 33 p. (no date).[3]

U.S. Environmental Protection Agency, "LMB/LiF Fusion of HWDS Solid-Phase and Nonaqueous Samples for Total Metals." U.S. EPA, National Enforcement Investigation Center, Denver, Colorado, Method 200.62. 3 p. (no date).[5]

1.1.2 Method Summary

A 100-mg sample is fused with lithium metaborate (LMB) and lithium fluoride (LiF) for 9 minutes at 975°C in a graphite crucible in a muffle furnace. After cooling, the fusion pellet is transferred to a polyethylene vial, dissolved in 100 ml 4-percent HNO_3, and filtered through a prewashed 0.45-μm membrane filter to remove any carbon from the graphite crucible that may have adhered to the pellet.

Simultaneous or sequential multi-element determination of trace elements in the acid solution is accomplished using the inductively coupled plasma (ICAP) spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are used to quantify the trace elements. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectal interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

1.1.3 Applicability

The method is primarily applicable to hazardous waste samples and has been successfully applied to high-silica soil, sediment, clay, sludge, ash, sulfide bearing ore, and oil. Because of the relatively low temperature used, volatile elements such as arsenic and lead may also be determined in the final solution.

1.1.4 Precision and Accuracy

The performance of the procedure for 25 metals in 11 standard reference materials is summarized in Table 2. The work was performed in a single laboratory.

1.1.5 Sample Preparation

Place the weighing dishes in a vacuum desiccator containing P_2O_5 and $CaSO_4$. Obtain and record a constant weight for these dishes.

Weigh an aliquot of wet HWDS solid-phase sample (approximately 1 g) into a pre-weighed dish. Place the samples in the desiccator and apply a vacuum.

After 48 hours of desiccation, reweigh the samples plus dishes. (A constant weight is obtained when two weighings separated by 6 hours agree to within 2 percent.) The percent moisture of the sample is calculated as:

$$\% \text{ moisture} = \frac{(\text{wet wt.}) - (\text{dry wt.})}{(\text{wet wt.})} \times 100$$

Place 6 to 8 graphite crucibles in a preheated muffle furnace and heat at 1,000°C for 30 minutes. Remove the crucibles; allow to cool slightly. Blow off excess graphite and chalky residue with compressed air.

Heat the crucibles for an additional 30 minutes at 1,000°C. Repeat the process of blowing off excess graphite and chalky residue with compressed air.

Store the prepared crucibles in a clean, closed container.

Prepare the lithium metaborate flux by combining 3 parts LiF and 7 parts $LiBO_2$ (by weight). Mix the mixture thoroughly and store in a tightly-sealed container as the flux is hygroscopic.

Preheat the muffle furnace to 795°C.

TABLE 2. COMPARISON OF FOUND VALUES FOR REFERENCE MATERIALS TO RECOMMENDED VALUES FOR THE FUSION PREPARATION[3]

Reference Material		Element							
		Ag	Al(%)	As	Ba	Be	Ca(%)	Co	Cr
USGS GXR-1	RV	31±2.8	3.54±0.25	460±30	560±120	1.12±0.17	0.87±0.08	9.3±1.1	10±2
	FV	44±5.2	3.4±0.02	370±29	660±11	ND	0.87±0.02	ND	13±4
USGS GXR-2	RV	<30	18.6±0.4	31±5	2000±400	1.64±0.09	0.82±0.04	9±2	37±10
	FV	ND	19. ±0.3	31±4	2200±39	ND	0.88±0.004	ND	31±6
USGS GXR-3	RV	<30	6.4±1.6	4000±450	4700±800	26±1	14.1±0.6	48±5	19±1
	FV	ND	6.7±0.1	3700±310	5300±28	23±2	15±0.04	42±4	19±2
USGS GXR-4	RV	<30	7.40±0.20	98±10	1350±330	2.1±0.2	0.90±0.05	16±2	64±10
	FV	ND	7.7	108	1700	ND	0.97	ND	64
USGS GXR-5	RV	<30	20.8±1.6	12±3	1800±500	1.19±0.16	0.75±0.06	30±5	100±5
	FV	ND	20. ±0.5	12	1900±50	ND	0.78±0.02	35±	100±3
USGS GXR-6	RV	<30	16.6±0.4	340±30	1100±300	1.1±0.1	0.097±0.01	14±3	96±10
	FV	ND	19±0.8	210±6	1600±100	ND	0.10±0.02	ND	82±0.2
USGS GSE	RV	380	7.2	450	500	500	3.75	450	490
	FV	340±8	7.0±0.2	310±51	495±9	470±9	3.6±0.06	420±14	450±21
NBS No. 1633	RV	NRV	12.7±0.5	61±6	2700±200	12.3±0.3	4.7±0.6	41.5±1.2	131±2
Flyash	FV	ND	12.3±0.1	59±3	2500±37	ND	4.4±0.01	52±10	120±3
NBS No. 1648	RV	NRV	3.5±0.1	115±10	740±60	NRV	5.8±0.5	17.6±0.5	403±12
Urban Part	FV	ND	3.5±0.05	110±5	730±13	ND	5.6±0.01	ND	390±3
NBS No. 1645	RV	NRV	NRV	66	NRV	NRV	NRV	8	29,600±2800
River Sed	FV	52±3	3.0±0.2	NA	405±20	ND	1.7±0.08	ND	23,000±2000
CONOSTAN	RV	500	500	NRV	500	NRV	500	NRV	500
Oil C-21	FV	130±160	340±3	NA	460±23	ND	500±84	ND	350±9.9
LIMIT OF DETECTION (ppm)		30.	100.	2.	2.	3.	300.	20.	10.

(Continued)

TABLE 2. (Continued)

Reference Material		Element								
		Cu	Fe(%)	K(%)	Mg(%)	Mn	Mo	Na	Ni	Pb
USGS GXR-1	RV	1300±10	24.7±1.8	0.053±0.009	0.21±0.01	970±230	NRV	550±110	42±10	670±20
	FV	1200±15	25±0.3	0.066±0.01	0.24±0.002	1000±46	ND	ND	ND	760±70
USGS GXR-2	RV	108±36	1.90±0.23	1.41±0.23	0.88±0.05	960±100	NRV	5540±200	18±3	615±15
	FV	89±8	1.9±0.01	1.50±	0.92±0.003	1100±2	ND	5800±180	ND	450±53
USGS GXR-3	RV	15	18.6±1.8	0.81±0.13	0.64±0.05	22,300±2000	NRV	7800±400	55±3	15±2
	FV	22±2	18±	0.84±	0.87±0.008	23,000±370	ND	7800±560	ND	ND
USGS GXR-4	RV	6500±200	2.97±0.43	4.3±0.6	1.65±0.05	140±20	310±25	5300±300	38±4	NRV
	FV	7100	3.0	4.5	1.8	160	250	5100	ND	ND
USGS GXR-5	RV	360±20	3.19±0.29	0.82±0.11	1.22±0.05	280±20	30±4	7700±300	63±7	22±2
	FV	380±10	3.5±0.05	1.1±0.02	1.3±0.02	340±5	ND	6700±160	ND	ND
USGS GXR-6	RV	105±12	5.58±0.42	2.04±0.25	0.62±0.04	1000±50	1.7±0.4	1040±60	22±4	110±10
	FV	76±9	5.4±0.05	2.00±0.04	0.69±0.02	1100±17	ND	840±450	ND	ND
USGS GSE	RV	500	4.6	1.3	2.2	600	500	34,000	500	500
	FV	470±16	4.6±0.1	NA	2.2±0.04	670±10	420±24	32,000±2000	510±13	380±34
NBS No. 1633	RV	120	6.2±0.3	1.61±0.15	1.8±0.4	493±7	36±5	3200±400	98±3	70±4
Flyash	FV	50±25	6.0±0.02	1.9±0.09	1.3±0.01	500±2	ND	2300±290	ND	ND
NBS No. 1648	RV	609±27	3.91±0.10	1.00±0.11	0.83±0.08	790±20	NRV	4000±200	82±3	6550±80
Urban Part	FV	330±11	3.8±0.03	1.1±0.06	0.79±0.007	800±6	ND	4300±240	72±11	5500±130
NBS No. 1645	RV	109±19	11.3±1.2	1.2	NRV	785±97	NRV	5500	45.8±2.9	714±28
River Sed	FV	120±20	11.3±0.4	NA	6000±70	940±40	ND	6100±700	73±8	345±60
CONOSTAN	RV	500	0.05	NRV	0.05	500	500	500	500	500
Oil C-21	FV	315±70	0.043±0.003	NA	0.050±0.004	490±27	420±20	ND	110±50.	350±34
LIMIT OF DETECTION (ppm)		10.	500.	200.	20.	2.	30.	500.	100.	100.

(continued)

TABLE 7. (Continued)

Reference Material		Element							
		Sb	Si(%)	Sr	Ti	V	Y	Zn	Zr
USGS GXR-1	RV	124±6	23.0±1.3	280±60	650±50	88±9	NRV	740±110	66±20
	FV	130±17	21±0.5	300±4	330±8	140±10	ND	1100±8	40±2
USGS GXR-2	RV	48±5	23.0±2.2	160±23	2800±300	57±20	NRV	500±60	200±40
	FV	41±3	2.0±0.04	160±1	3100±22	64±4	ND	580±60	290±4
USGS GXR-3	RV	40±3	6.1±1.4	1140±100	1000±10	39±10	NRV	220±70	NRV
	FV	29±3	6.7±0.06	1103±19	1130±13	77±5	ND	300±19	98±3
USGS GXR-4	RV	4.4±0.8	31.3±2.1	220±30	2600±300	92±15	NRV	54±10	200±40
	FV	3±4	29.	240	2900	92	11	ND	NA
USGS GXR-5	RV	2±1	19.7±1.2	120±20	2100±300	60±20	NRV	50±5	140±20
	FV	ND	19. ±0.2	110±2	2600±16	64±6	ND	ND	170±1
USGS GXR-6	RV	3.8±0.7	22.9±1.7	42±9	5000±400	180±20	NRV	120±20	106±8
	FV	ND	19±0.4	47±2	5300±110	210±10	ND	ND	130±6
USGS GSE	RV	470	29	500	490	500	490	500	480
	FV	480±25	26±0.4	530±12	600±43	570±96	450±13	600±14	500±11
NBS No. 1633	RV	6.9±0.6	21±2	NRV	7400±300	214±8	NRV	210±20	301±20
Flyash	FV	ND	18±0.1	NA	7600±7[illegible]	250±2	59±1	220±3	292±16
NBS No. 1648	RV	45±3	12.5±0.2	NRV	4000±200	130±7	NRV	4760±140	NRV
Urban Part	FV	40±4	10±0.1	220±6	4200±21	140±2	ND	5900±14	170±8
NBS No. 1645	RV	51	23.8	NRV	NRV	23.5±6.9	NRV	1720±169	NRV
River Sed	FV	NA	23±0.5	NA	NA	54. ±6.	ND	1900±50	NA
CONOSTAN	RV	NRV	500	NRV	500	500	NRV	500	NRV
Oil C-21	FV	NA	ND	ND	NA	440±23	ND	390±46	NA
LIMIT OF DETECTION (ppm)		3.	300	2.	30.	10.	3.	60.	20.

RV = Recommended Value
FV = Found Value
NRV = No RV Given
ND = Less Than Limit of Detection
NA = Not Analyzed

Note 1. As and Sb determined by HGA-AAS.
Note 2. K, Sr, Ti and Zr measured on N + 1 channel.
Note 3. Se and Cd are volatilized during the fusion preparation.

Tare the prepared crucible. Weigh 1.0 g LMB flux into the crucible. Weigh 0.100 g dry sample into the flux. Carefully stir the contents of the crucible with a platinum wire to mix the sample and the flux. Distribute the mixture evenly in the crucible.

Using tongs, place the crucible in the furnace. Fuse the sample for 5 minutes. Check the sample after 5 minutes (for splattering, etc.) and mix. Return the sample to the furnace and fuse for an additional 4 minutes (total fusion time is 9 minutes).

Remove the crucible and place on a cinder plate to cool. After the fusion product has cooled, transfer the pellet to an 8-ml polyethylene vial by tapping the bottom of the crucible.

Dissolve the pellet in 100 ml 4-percent v/v HNO_3. After dissolution is complete, filter the sample through a prewashed 0.45-µm membrane filter to remove any carbon from the graphite crucible that may have adhered to the pellet.

1.1.6 Sample Analysis

Establish proper instrument operating conditions. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 minutes of operation prior to calibration.

Initiate the appropriate operating configuration of the computer.

Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Subsection E.4. Flush the system with the calibration blank (Subsection E.5.1) between each standard.

NOTE: For boron concentrations greater than 500 µg/l, extended flush times of 1 to 2 minutes may be required. (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±5 percent (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

Flush the system with the calibration blank solution

(Subsection E.5.1) between each sample. Analyze the instrument check standard (Subsection E.6.1) and the calibration blank (Subsection E.5.1) after every tenth sample.

If it has been found that the method of standard additions is required, the following procedure is recommended.

The standard additions technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration c_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration c_X is calculated:

$$c_X = \frac{S_B V_S c_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and c_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus c_S is much greater than c_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

For the results from this technique to be valid, the following limitations must be taken into consideration:

a. The analytical curve must be linear.

b. The chemical form of the analyte added must respond the same as the analyte in the sample.

c. The interference effect must be constant over the working range of concern.

d. The signal must be corrected for any additive interference.

2.1 Determination of Metals in Aqueous Samples Using Inductively Coupled Plasma-Atomic Emission Spectrometric Analysis

Analytical Procedure: evaluated
Sample Preparation: available

2.1.1 Reference

U.S. Environmental Protection Agency, "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes." U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. Method 200.7., 31 p. (November 1980).

2.1.2 Method Summary

The method describes a technique for the simultaneous or sequential multi-element determination of trace elements in aqueous solution. Dissolved elements are determined directly in filtered, acidified samples. Suspended solids filtered from the original sample are digested using nitric acid, the digest is taken up in hydrochloric acid and analyzed. Total element concentrations are determined in a nitric acid digest of the whole sample.

The basis of the analytical method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences specified in Subsection C (and tests for their presence) should also be recognized and appropriate correcti made.

2.1.3 Applicability

This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters.

Dissolved elements are determined in filtered, acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/l.

Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects.

Table 3 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent, and as the sample matrix varies, these concentrations may also vary.

2.1.4 Precision and Accuracy

In an EPA round-robin study[1], seven laboratories applied the ICP technique to acid/distilled water matrices that had been spiked with various metal concentrates. The results of this study are listed in Table 4.

2.1.5 Sample Preparation

For the determination of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. If a precipitate forms upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described below.

For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-ml Griffin beaker and add 4 ml conc. HNO_3. Cover the beaker with a watch glass and heat gently. After the membrane has dissolved, increase the temperature of the hot plate. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by the light color of the digest. Evaporate to near dryness (2 ml), cool, add 10 ml HCl (1+1) and 15 ml deionized, distilled water per 100 ml of final solution and warm the beaker gently for 15 minutes to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized, distilled water and filter the sample to remove insoluble material that could clog the nebulizer. Adjust the volume based on the expected concentrations of elements present. The sample is now ready for analysis. Concentrations determined on this digest shall be reported as "suspended."

TABLE 3. RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength, nm[a]	Estimated Detection Limit, µg/l[b]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see[c]
Selenium	196.026	75
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see paragraph 4.1.1).

[b]The estimated instrumental detection limits as shown are taken from Reference 4. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

TABLE 4. ICP PRECISION AND ACCURACY DATA[1]

Element	Sample No. 1 True Value µg/l	Sample No. 1 Mean Reported Value µg/l	Sample No. 1 Mean Percent RSD	Sample No. 2 True Value µg/l	Sample No. 2 Mean Reported Value µg/l	Sample No. 2 Mean Percent RSD	Sample No. 3 True Value µg/l	Sample No. 3 Mean Reported Value µg/l	Sample No. 3 Mean Percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

[1]Not all elements were analyzed by all laboratories.

NOTE: If the sample analysis solution has a different acid concentration from that given below, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

For the determination of total elements, choose a measured volume of the well-mixed, acid-preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker.

NOTE: If low concentrations of boron are critical, quartz glassware should be used.

Add 3 ml conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5-ml portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add 10 ml (1+1) HCl and 15 ml deionized, distilled water per 100 ml of final solution and warm the beaker gently for 15 minutes to dissolve any precipitate or residue. Allow to cool, wash down the beaker walls and watch glass with deionized, distilled water and filter the sample to remove insoluble material that could clog the nebulizer. Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis. Concentrations so determined shall be reported as "total".

For the determination of total recoverable elements, choose a measured volume of a well-mixed, acid-preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. Add 2 ml (1+1) HNO_3 and 10 ml (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 ml making certain the sample does not boil. Cool the sample and filter to remove insoluble material that could clog the nebulizer. Adjust the volume to 100 ml and mix. The sample is now ready for analysis. Concentrations determined on these digests shall be reported as "total".

2.1.6 Sample Analysis

Establish proper instrument operating conditions. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 minutes of operation prior to calibration.

Initiate the appropriate operating configuration of the computer.

Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Subsection E.4. Flush the system with the calibration blank (Subsection E.5.1) between each standard.

NOTE: For boron concentrations greater than 500 µg/l, extended flush times of 1 to 2 minutes may be required.

Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±5 percent (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

Flush the system with the calibration blank solution (Subsection E.5.1) between each sample. Analyze the instrument check standard (Subsection E.6.1) and the calibration blank (Subsection E.5.1) after every tenth sample.

If it has been found that the methods of standard additions is required, the following procedure is recommended.

The standard additions technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration c_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration c_X is calculated:

$$c_X = \frac{S_B V_S c_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and c_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus c_S is much greater than c_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

For the results from this technique to be valid, the following limitations must be taken into consideration:

a. The analytical curve must be linear.

b. The chemical form of the analyte added must respond the same as the analyte in the sample.

c. The interference effect must be constant over the working range of concern.

d. The signal must be corrected for any additive interference.

H. CALCULATIONS

Subtract average reagent blank values from the raw analytical value for each sample. This is particularly important for digested samples requiring large quantities of acid to complete the digestion.

If dilutions were performed on the samples or the sample digests, the appropriate value must be applied to the sample concentrations.

The concentration of aqueous samples, after correction for reagent blank and dilutions, is read directly from a standard curve. Report concentrations as either dissolved or total, depending on the method of sample preparation.

For solid-phase samples, multiply the concentration of the digest by the volume of the digest and divide by the original weight of sample digested.

$$\text{Solid Conc. (mg/g)} = \frac{(X)\ (V)}{(W)}$$

where:

X = concentration in the digest, mg/l

V = volume of digest, (0.1 l as written)

W = dry weight of sample, g.

If it is necessary to know the concentration on a wet-weight basis, divide the dry-weight concentration by the percent solids in the original sample.

REFERENCES

1. U.S. Environmental Protection Agency. "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes." U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. Method 200.7, 31 p. (November 1980).

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4. Winge, R. K., V. J. Peterson, and V. A. Fassel. "Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines." U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. EPA-600/4-79-017 (1979).

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